



COOPERATING TO IMPLEMENT THE GREAT LAKES WATER QUALITY AGREEMENT
MIS EN OEUVE DE L'ACCORD SUR LA QUALITE' DE L'EAU DES GRANDS LACS

Technical Summary of Progress under the Integrated Atmospheric Deposition Program 1990-1996

**U.S./Canada
IADN Scientific Steering Committee**

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ABSTRACT

This report is a technical summary of the progress made under the Integrated Atmospheric Deposition Network (IADN). IADN is a joint U.S. - Canada monitoring and research program which has been in operation since January, 1990. The report details the history of the formation of IADN, its mandate under the Great Lakes Water Quality Agreement and other legislated needs, and a brief technical summary of the results of the program. The report describes the Network, the rationale for the position and number of its existing sites, the chemicals for which it monitors, and the quality assurance program which ensures the integrity of the data produced. The atmospheric trends in air and precipitation concentrations seen in the Network are discussed and it is apparent that downward trends in concentrations for most semi-volatile organic compounds (SVOCs) and trace metals are seen at all sites which have longer than a three year record. Loading estimates of the amounts of these chemicals coming from the atmosphere to the lakes and volatilizing from the lakes have been made every two years during the program. These estimates are reviewed. The results show that the lakes are very sensitive to the atmospheric concentration of the chemicals, and this points out the fragility of these resources given long-range transport of toxic chemicals globally. The results also are interpreted in terms of air trajectory analyses and other statistical tests which give information on source-receptor identification. These techniques identify many of the SVOCs as potentially coming from outside the Great Lakes basin, while some of the currently anthropogenically-released substances, such as the PAHs and trace elements, have in-basin sources.

Finally, the report suggests ways in which the next phase of IADN could be defined. These suggestions will be reviewed in late 1997, using a peer review panel, and provide the basis for a Second Implementation Plan for IADN, expected to cover the period 1998-2004.

TABLE OF CONTENTS**PAGE**

I. History and Mandates	8
I.1 History of the Integrated Atmospheric Deposition Network (IADN)	8
I.2 The Present Goals of IADN's Implementation Plan (1990).....	10
I.3 IADN Mandates.....	12
I.3.1 Annex 15 GLWQA.....	12
I.3.2 Clean Air Act Amendments of 1990.....	12
II. Results.....	13
II.1 Current Status of the Network.....	13
II.1.1 Chemicals.....	13
II.1.2 IADN Sites	22
II.1.3 Siting Criteria	28
II.1.4 Sampling/Analysis Protocols - Methods Development	29
II.1.5 Quality Assurance/Quality Control	34
II.1.6 Data Status	38
II.2 Temporal Trends of Organochlorines Near the Great Lakes.....	38
II.2.1 Gas-Phase Concentrations.....	38
II.2.1.1 Temperature Effects	38
II.2.1.2 Temporal Trends in PCBs	43
II.2.1.3 Temporal Trends in Pesticides	47
II.2.2 Spatial and Temporal Trends in Organic Precipitation Concentrations	50
II.3 Loading Results from the IADN data.....	61
II.4 Extensions to IADN Data Analyses - Identification of Potential Sources	77
II.4.1 Air trajectory analyses.....	77
II.4.2 Potential Source Contribution Function and Principal Component Analyses	85
III. Where does IADN go from here?	87
III.1 Goal of the Second Implementation Plan (IP2)	87
III.2 Unresolved issues under IP1	88
III.3 Recommendations for IP2.....	90
III.3.1 Recommendations to improve measuring and reporting	90
III.3.2 Recommendations to improve our understanding of atmospheric processes	92
IV. References	94

Note that colour plates are printed single sided on odd-page numbers, the reverse side is left intentionally blank and the following even page number is not printed.

LIST OF TABLES**PAGE**

Table I-1: IPI Chemical List.....	11
Table II-1: Organochlorine Compounds Measured by Agency	15
Table II-2: Polychlorinated Biphenyls Measured by Agency and Medium	16
Table II-3: Polynuclear Aromatic Hydrocarbon Measured by Agency and Medium.....	19
Table II-4: Limits of detection for air and precipitation trace metal concentration measurements	20
Table II-5: Additional Trace Elements Measured by Agency and Medium.....	21
Table II-6: IADN Master Station Locations	22
Table II-7: Satellite facilities under IADN.....	24
Table II-8: Current data status by agency	39
Table II-9: The Half-lives of PCBs in Various Environmental Compartments.....	45
Table II-10: Atmospheric half-lives and relative standard errors (RSE) of pesticides.....	48
Table II-11: Concentration Data from IADN Master Stations Annual Averages.....	63
Table II-12: Intercomparison of Loading Estimates for the Great Lakes (kg y^{-1})	67
Table II-13: Fluxes of Semivolatile Organic Compounds to the Great Lakes	68
Table II-14: Fluxes of Trace Elements to the Great Lakes	69
Table II-15: Varimax Rotated Principal Components, 1990-1994 Point Petre Trace Elements and PAH data.....	86

LIST OF EQUATIONS

Equation II-1: Clausius-Clapeyron Equation	41
Equation II-2: Time-temperature trend regression	44
Equation II-3: Correction of partial pressure to ambient temperature.....	49
Equation II-4: Loading equations	61

LIST OF FIGURES

Figure II-1: Locations of current sampling stations	26
Figure II-2: Fluctuation in the gas-phase concentrations of total PCBs over time.	41
Figure II-3: Clausius-Clapeyron plots relating the natural logarithm of the partial pressure.	43
Figure II-4: First order decay of α -HCH at Sturgeon Point.....	50
Figure II-5: α -HCH concentration in precipitation.....	51
Figure II-6: γ -HCH concentration in precipitation.....	51
Figure II-7: Dieldrin precipitation concentration time series	53
Figure II-8: Endosulphan trends in precipitation for Superior, Erie and Ontario.....	55
Figure II-9: Concentrations of atrazine in precipitation.....	57
Figure II-10: Concentrations of metolachlor in precipitation.....	59
Figure II-11: Percentage of the deposition to the lake	65
Figure II-12: Wet deposition, dry deposition, gas absorption and gas volatilization	71
Figure II-13: As for Figure II-12, except for the PCB congeners.	73
Figure II-14: Wet and dry deposition for the PAHs and trace metals by lake for the 1993 year.	75
Figure II-15: Back trajectories at 850 mb showing potential sources of toxaphene.....	79
Figure II-16: Back trajectories at 850 mb showing potential sources of p,p'-DDT.	79
Figure II-17: Back trajectories for approximately the top 10 th percentile of concentrations.....	81
Figure II-18: 1000mb back trajectories for approximately the top 10th percentile of concentrations	83

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LIST OF ACRONYMS

AEOLOS	Atmospheric Exchange over Lakes and Oceans Study
AES	Atmospheric Environment Service, Environment Canada
B(a)P	Benzo(a)pyrene
BGLTS	Bi-national Great Lakes Toxics Strategy
CAA	U.S. Clean Air Act
CAPMoN	Canadian Air and Precipitation Monitoring Network
COA	Canada Ontario Agreement
DDT	1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane
DQI	Data quality indicator
EC	Environment Canada
ECD	Electron capture detector
EDXRF	Energy dispersive x-ray fluorescence
EHD	Ecosystem Health Division
EMEP	European Monitoring and Evaluation Project
EPA	Environmental Protection Agency (U.S.)
GC	Gas chromatography
GFAAS	Graphite furnace atomic absorption spectroscopy
GLWQA	Great Lakes Water Quality Agreement
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
HPLC	High pressure liquid chromatography
IADN	Integrated Atmospheric Deposition Network
ICP-MS	Inductively coupled plasma-mass spectrometry
IDL	Instrument detection limit
IIT	Illinois Institute of Technology (Chicago, IL)
IJC	International Joint Commission
IP1	IADN First Implementation Plan
IP2	IADN Second Implementation Plan
ISWS	Illinois State Water Survey
IU	Indiana University
LaMP	Lakewide Management Plan (a GLWQA initiative)
LMUATS	Lake Michigan Urban Air Toxics Study
LOD	Level of detection
MOE	Ministry of Environment (Ontario)
MDL	Method detection limit
MIC	Meteorological Instruments Corporation
NAA	Neutron activation analysis
NAFTA-CEC	North American Free Trade Agreement - Commission for Environmental Cooperation
NATCHEM	National Atmospheric Chemistry Database
NCP	Northern Contaminants Program
NOAA	National Oceanographic and Atmospheric Administration (U.S.)
NWRI	National Water Research Institute
OC	Organochlorine
MOE	Ontario Ministry of Environment and Energy
OP	Organophosphate
PAHs	Polynuclear aromatic hydrocarbons
PCA	Principal component analysis
PCBs	Polychlorinated biphenyls
PUF	Polyurethane foam
QA/QC	Quality assurance/quality control
QAPjP	Quality Assurance Project Plan
QAPP	Quality Assurance Program Plan
RAP	Remedial Action Plan (a GLWQA initiative)
RDMQ	Research Data Management and Quality Control System
RSE	Relative standard error
SPM	Standard Procedures Manual
SVOC	Semi-volatile organic compounds
TEOM	Tapered element oscillating microbalance (Rupprecht and Paternick, Inc.)
TOC	Total organic carbon
TSP	Total suspended particulate
UNECE	United Nations Economic Commission for Europe
XAD	A proprietary absorbent resin

I. History and Mandates

I.1 History of the Integrated Atmospheric Deposition Network (IADN)

The atmospheric deposition of persistent toxic chemicals to the Great Lakes was first observed in rainfall by Sanderson and Frank (1977) followed rapidly by Murphy and Rzeszutko (1977), Swain (1978) and Strachan and Huneault (1979). Initial focus was on PCBs, and the observed concentrations, coupled with annual rainfall deposition, indicated inputs of several tonnes per lake. Other contaminants were found at much reduced levels although all were near the detection limits at that time.

In the mid-1980s, the early success of the control programs of the late 1970s and early 1980s to lower contaminant levels in fish seemed to be ending. Monitoring of levels in fish and other biota noted that a downward trend of contaminant concentration appeared to be leveling out. Early studies assessed by the International Joint Commission (IJC) under the Great Lakes Water Quality Agreement (GLWQA) had previously mentioned the role that the atmosphere might play in maintaining high lake concentrations.

The IJC and its Science Advisory and Water Quality Boards sought an explanation for the lack of continued reduction in the contaminant levels in biota. Examination of lake water and tributaries had been insufficient to explain the sources of the continuing contamination. One such explanation was the possibility that the contaminants were coming via the atmosphere. This underlined the need for an atmospheric component for the Great Lakes International Surveillance Plan.

In 1986, an IJC Workshop in Scarborough (Toronto) Canada examined 14 chemicals for the importance of their atmospheric inputs, relative to other identified sources. The existing data at the time proved to be very "patchy" -- there were whole water concentrations from one corner of one lake during one particular season of a particular year and this was compared with filtered water concentrations from another venue four years later. Air data, if available at all, often came from cities and were of questionable value for assessing open-lake inputs. Data on direct discharges to the lakes were very limited and concentration data for the organics in tributary and connecting channel waters were almost non-existent. The workshop determined that the data for only

four chemical classes and compounds - PCBs, DDT, B(a)P and Pb -- warranted the exercise of undertaking a mass balance and even these were felt to carry a high level of uncertainty because of insufficient data. There was also concern that few data existed on emissions of the study compounds despite their known toxicity.

The Workshop Report (Strachan and Eisenreich, 1988) concluded that the atmosphere was indeed a major source of the contaminants of concern, particularly for the upper Great Lakes. The report provided scientific support for the inclusion of a separate Annex (#15) in the "Protocol" revision to the 1978 GLWQA (1987 Revision).

At the same time as the Protocol revisions were being developed, the IJC Water Quality Board's Surveillance Work Group created a Task Force to prepare a plan for accomplishing the surveillance aspects of what was then in the draft Protocol. The "Plan" (IJC, 1988), outlined the need for 17 investigations on measurement and process-related subjects. The Task Force Report in 1988 formed the basis for subsequent development of IADN. The management of the process, however, was transferred to "the Parties" in the Protocol and thereafter the IJC played a smaller role in determining the atmospheric input of persistent toxic substances to the lakes.

In 1989, the Canada-Ontario Agreement created an Air Toxics Committee under Atmospheric Environment Service (AES) leadership, and this group developed plans to implement Annex 15 and the Task Force recommendations on the Canadian side. The Canadian effort identified which chemicals should be monitored, what the criteria for an IADN site should be, what equipment would be needed, and what QA/QC programme was needed. Liaison with the EPA's Great Lakes National Program Office was initiated and a meeting was held in Detroit on December 4-5, 1989 to agree on details for a programme -- for IADN and potentially for Annex 15. The outcome of that meeting was the formation of three working group reports which further defined the IADN network activities. In early 1990, the process was formalized with a signed 6-year Implementation Plan (Egar and Adamkus, 1990).

The first IADN station to be initiated was Point Petre, on the north shore of Lake Ontario -- in November 1988. A station at Green Bay (Lake Michigan) was opened in 1989, but this location was re-sited to Eagle Harbour on the Keewenaw Peninsula (Lake

Superior) in 1990. The official designation for the commencement of IADN was January 1990. Stations at Sturgeon Point (Lake Erie), Burnt Island (Lake Huron) and Sleeping Bear Dunes (Lake Michigan) followed in 1991-92.

I.2 The Present Goals of IADN's Implementation Plan (1990)

The first Implementation Plan (IP1) for the IADN was signed for "the Parties" by D. L. Egar (for Canada) and V. V. Adamkus (for the U.S.) in June, 1990. It took, as its stated objective, the acquisition of "... sufficient, quality assured data to estimate with a specified degree of confidence the loading to the Great Lakes Basin of selected toxic substances". Elsewhere in IP1, it is clear that the purpose of this objective is to determine the relative importance of the atmospheric pathway. While IADN is intended to estimate the relative loadings of the identified chemicals, IP1 also acknowledged the report of the IJC's Atmospheric Deposition Task Force outlining many critical research issues and the fact that these needed resolution "... in order to understand and quantify the importance of the atmospheric pathway for toxic substances.". In IP1, however, research -- other than equipment needs and method development -- was not addressed.

The goals for IADN, taken from the directions that IP1 provided to the IADN researchers, were to:

- identify which chemicals were to be investigated and to monitor atmospheric deposition,
- define the number and the local criteria for siting of sampling locations,
- describe the sampling and analytical methodology, and
- develop a quality assurance/control plan to ensure data comparability.

The IP1 itself identified the chemicals to be investigated (Table I-1). The list was short and intended to be a limited, representative spectrum of persistent toxic substances rather than comprehensive; a secondary -- and longer -- tier of organochlorine pesticides was also given on the understanding that these could be determined with additional effort. Other compounds (Tier 3), notably the chlorobenzenes, additional PAHs, co-planar PCB congeners and toxaphene were identified as important potential additions to the analyte list but for which additional methodological development was needed. "New" chemicals, particularly large volume agrochemicals, were identified for potential study.

Table I-1: IP1 Chemical List

IP1 Tier 1 “Achievable” chemicals and classes
PCBs (total and congeners) α - HCH γ - HCH Benzo(a)pyrene Pb
IP1 Tier 2 “Method Development Needed”
Σ DDT Chlordane Nonachlor Heptachlor epoxide Methoxychlor Dieldrin Hexachlorobenzene Endrin As Se Cd Hg
IP1 Tier 3 “Extensive Methodology Development Needed”
Chlorobenzenes PAHs Toxaphene co-planar PCBs Dioxins/Furans Agrochemicals Industrial chemicals

Originally, the IP1 instructed the IADN researchers to establish one "master" station and up to four "satellite" stations per lake plus “upwind and downwind” sites (totaling of a maximum of 22 satellite stations). The satellite stations were originally identified in the IJC's Plan to provide a broader geographic coverage than that provided by single sites on each lake. IP1 predicted the installation of 11 satellite stations in the second two years of the program and 11 more during the third two year period. There has been no quantitative assessment of the requirement for, and the desired placement of, these stations. A discussion of satellite facilities is given in Section II.

In addition to the number of stations, criteria for the local condition of the stations were to be defined. The IP1 directed that the stations were to be as close to the lakes as

possible, proximity to urban centres was generally to be avoided, and that further local site criteria were to be identified.

In the case of the sampling and analytical methodology, the directions (and IADN goals) were most specific for the list of equipment to be employed at each master although it was left open whether these could be changed. Beyond this, the direction given was only to exchange documentation for the several agency sampling and analytical protocols and to ensure data comparability. The QA/QC program was implied as the mechanism for this latter.

The IP1 directed, in some detail, that IADN would prepare and individual agencies would adhere to a quality assurance program. Everything prescribed for this was designed to ensure data comparability among the various agencies that would participate in the two countries and which would contribute their data to a common data base to be established. The IP1 recommended that the implementation of this sub-program be accomplished with the appointment of a QA Manager.

I.3 IADN Mandates

I.3.1 *Annex 15 GLWQA*

Annex 15 of the Great Lakes Water Quality Agreement (the 1987 Protocol) is reproduced in its entirety in Appendix A. The Parties are committed to carrying out the requirements of the GLWQA and its Annexes. Item 3 of Annex 15 clearly provides a direct mandate for the existing IADN program. Items 2(b) and 4 are not related to the work activities of IADN.

The rest of the research mandate (items 2(a) and 2(c)) has been the topic of considerable discussion during the IP1 period. It is the direction of IADN program management that this Summary be a review of IADN and not Annex 15. By that definition, IADN is a crucial part of Annex 15 but it is not Annex 15. The partially addressed research mandate of Annex 15 will be discussed in Section III.2.

I.3.2 *Clean Air Act Amendments of 1990*

The United States Congress passed the Amendments to the U.S. Clean Air Act (CAA) of 1990. Section 112(m) directs EPA, in cooperation with the National Oceanic

and Atmospheric Administration (NOAA), to identify and assess the extent of atmospheric deposition of toxic pollutants to the Great Waters. As part of the assessment, EPA undertakes the following activities (rearranged from EPA's presentation to coincide with those of the Annex 15 requirements):

- (i) research for developing and improving monitoring methods and for determining the relative contribution of atmospheric pollutants to total pollutants in the Great Waters, and investigation of sources and deposition rates of air pollutants,
- (ii) evaluation of adverse human health and environmental effects,
- (iii) monitoring of atmospheric deposition, including the establishment of monitoring networks in the Great Lakes and other locations,
- (iv) determination of whether regulatory programs under section 112 are "adequate to prevent serious adverse effects to public health and serious or widespread environmental effects" associated with atmospheric deposition to the Great Waters. Based on this determination, EPA is directed to take additional measures that are necessary and appropriate to prevent such adverse effects to human health and the environment, to identify of exceedences of water quality standards, to sample fish and wildlife for atmospherically-deposited pollutants and to characterize the sources of such pollutants.

It is clear that many of the above activities are very similar to those of the Annex 15 and IADN requirements. The same considerations and limitations apply including those of funding. Scientific results from IADN activities can also serve to provide some of the input required by the CAAA (112) at least for the Great Lakes Region.

II. Results

II.1 Current Status of the Network

II.1.1 Chemicals

IADN has succeeded in making measurements of all the chemicals on the primary and secondary target lists of IP1, except Hg. In addition, at the end of the first

implementation plan, research efforts at IADN sites have examined toxaphene, co-planar PCBs, Hg, and some herbicides; however, there has been no inclusion of these chemicals onto the routine monitoring list.

Tables II.1 (Organochlorine Compounds - less PCBs), II.2 (PCBs), II.3 (PAHs) and II.4 (Trace elements) show the list of chemicals monitored by each agency and the medium in which they are measured (air or precipitation). In addition, Table II.5 shows a number of trace elements which are also monitored. IDL and LODs have not yet been set for these latter elements in the IADN Quality Assurance Program Plan (QAPP).

Table II.1 and II.3 are unambiguous in the assignment of peaks and nomenclature. The polychlorinated biphenyls are much more difficult to compare between agencies. Table II.2 shows that many congeners (the emboldened values in the Research Data Management and Quality Control system, RDMQ, see section II.4, nomenclature) co-elute on one type of column and are separated on other columns. Thus, different agencies will have differences in the congener reporting. The question of PCB targets will be addressed in section III. Clearly, the non-unique nature of these identifications is a problem which needs rectification during the IP2 period.

Table II-1: Organochlorine Compounds Measured by Agency

RDMQ Stand. Name	CAS Number; Alt. Name	AES Vapour	EHD Precip.	IU Precip.	IU Part.	IU Vapour	NWRI Precip.
A_HCH	319-84-6	x	x	x	x	x	x
B_HCH	319-85-7	x					x
D_HCH	319-86-8	x					
G_HCH	58-89-9; Lindane	x	x	x	x	x	x
ALDRIN	309-00-2	x	x				x
DIELD	60-57-1	x	x	x	x	x	x
ENDRIN	70-20-8	x	x				x
T_CHLOR	5103-74-2; trans-chlordane; γ -chlordane	x	x	x	x	x	x
C_CHLOR	5103-71-9; cis-chlordane; α -chlordane	x	x	x	x	x	x
T_NONA	39765-80-5	x		x	x	x	
OXYCHLR	26880-48-8	x					
HEPTCHL	76-44-8	x	x				x
HEPTEPO	1024-57-3	x	x				x
MIREX	2385-85-5	x					x
PHOTMIR	39801-14-4	x					
A_ENDOS	959-98-8; a-endosulfan	x	x				x
B_ENDOS	33213-65-9; b-endosulfan	x	x				x
OP_DDT	784-02-6; 1,1,1-trichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl)ethane	x	x				
PP_DDT	50-29-3; 1,1,1-trichloro-2,2-bis(para-chlorophenyl)ethane	x	x	x	x	x	x
OP_DDD	53-19-0 1,1-dichloro-2 (o-chlorophenyl)- 2(p-chlorophenyl) ethane	x					
PP_DDD	72-54-8; 1,1-dichloro-2,2-bis(p-chlorophenyl)-ethane	x	x	x	x	x	x
PP_DDE	72-55-9; 1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene	x	x	x	x	x	x
METHOXY	72-43-5; methoxychlor	x	x				
HCB	118-74-1; hexachlorobenzene	x	x	x	x	x	x

Table II-2: Polychlorinated Biphenyls Measured by Agency and Medium

(emboldened names are ones for which non-unique identifiers exist;
primarily due to congener overlap in chromatograms, A,B,C refer to different interferences)

RDMQ Stand. Name	Alternate Name	AES Vapour	EHD Precip.	IU Precip.	IU Part.	IU Vapour	NWRI Precip.
PCBs:							
P001		x					
P003		x					x
P004_A	4+10	x		x	x	x	x
P005		x					
P005_A	5+8			x	x	x	x
P006		x		x	x	x	x
P007		x					x
P007_A	7+9			x	x	x	
P008		x					
P012_A	12+13	x					x
P012				x	x	x	
P013				x	x	x	
P014				x	x	x	
P015		x					
P016		x		x	x	x	x
P017_A	17+15			x	x	x	
P017		x					x
P018		x		x	x	x	x
P019		x		x	x	x	x
P022		x		x	x	x	x
P024_A	24+27	x					x
P024				x	x	x	
P025		x		x	x	x	x
P026		x		x	x	x	x
P027				x	x	x	
P028		x		x	x	x	x
P029		x		x	x	x	
P030		x		x	x	x	
P031		x		x	x	x	x
P032		x		x	x	x	x
P033_A	33+53	x					x
P033				x	x	x	
P037_A	37+42	x					
P037				x	x	x	
P040		x		x	x	x	x
P041_A	41+64+71						x
P041_B	41+64	x					
P041_C	41+71			x	x	x	
P042				x	x	x	x
P043		x		x	x	x	
P043_A	43+49						x
P044		x		x	x	x	x
P045		x		x	x	x	x
P046		x		x	x	x	x
P047_A	47+48	x					
P047				x	x	x	x
P048				x	x	x	x
P049		x		x	x	x	
P051		x		x	x	x	
P052		x		x	x	x	x
P053				x	x	x	
P056_C	56+60			x	x	x	x
P056_B	56+92	x					

P060		x					
P061		x					
P063				x	x	x	x
P064				x	x	x	
P065				x	x	x	
P066				x	x	x	x
P070		x					
P070_A	70+76			x	x	x	x
P071		x					
P074		x		x	x	x	x
P075		x					
P076		x					
P077				x	x	x	
P081				x	x	x	
P082				x	x	x	x
P083		x		x	x	x	x
P084		x					
P084_A	84+92			x	x	x	x
P085		x		x	x	x	x
P087_A	81+87	x					x
P087				x	x	x	
P089		x		x	x	x	x
P091		x		x	x	x	x
P095_A	95+96	x					
P095				x	x	x	x
P097		x		x	x	x	x
P099		x		x	x	x	x
P100		x		x	x	x	x
P101		x		x	x	x	x
P105		x					
P105_A	105+132+153			x	x	x	x
P107_A	107+147	x					
P107				x	x	x	x
P110_A	110+77	x					
P110				x	x	x	x
P114		x					
P114_A	114+131			x	x	x	
P118		x		x	x	x	x
P119		x		x	x	x	x
P123		x					
P123_A	123+149			x	x	x	
P124		x					
P124_A	124+135+149						x
P126		x					
P128_A	128+67	x					
P128				x	x	x	x
P129		x		x	x	x	x
P130		x		x	x	x	
P131		x					
P132		x					
P134		x		x	x	x	
P134_A	134+143						x
P135_B	135+124	x		x	x	x	
P136		x		x	x	x	x
P137		x					x
P137_A	137+176			x	x	x	
P138		x					
P138_A	138+163			x	x	x	x
P141		x		x	x	x	x
P146				x	x	x	x
P149		x					
P151_A	151+82	x					
P151				x	x	x	x

P153		x					x
P155		x					
P156				x	x	x	
P157	157						x
P157_B	157+173	x					
P157_A	157+200			x	x	x	
P158		x		x	x	x	x
P163		x					
P166		x		x	x	x	
P167				x	x	x	x
P169		x					
P170		x					x
P170_A	170+190			x	x	x	
P171_A	171+202+156						x
P171_B	171+156	x					
P172		x		x	x	x	x
P173				x	x	x	
P174		x		x	x	x	x
P175				x	x	x	x
P177		x		x	x	x	x
P178		x		x	x	x	x
P180		x		x	x	x	x
P182		x					
P182_A	182+187			x	x	x	x
P183		x		x	x	x	x
P185		x		x	x	x	x
P187		x					
P189		x		x	x	x	x
P190		x					x
P191		x		x	x	x	x
P193		x		x	x	x	x
P194		x		x	x	x	x
P195		x					
P196		x		x	x	x	
P197				x	x	x	x
P198		x		x	x	x	x
P199		x		x	x	x	x
P200		x					
P201		x		x	x	x	x
P202		x					
P202A	202+171			x	x	x	
P203		x		x	x	x	
P203_A	196+203						x
P204		x		x	x	x	
P205		x		x	x	x	x
P206		x		x	x	x	x
P207		x		x	x	x	x
P208		x					
P208_A	208+195			x	x	x	x
P209		x		x	x	x	
SUM PCB				x	x	x	

Table II-3: Polynuclear Aromatic Hydrocarbon Measured by Agency and Medium

PAHs: RDMQ Stand. Name CAS Number; Alt. Name		AES Vapour	EHD Precip	IU Precip	IU Part.	IU Vapour	NWRI Precip
ACENY	208-96-8; Acenaphthylene	x	x	x	x	x	
ACEN	83-32-9; Acenaphthene	x	x	x	x	x	
FLUOR	86-73-7; Fluorene	x	x	x	x	x	
PHEN	85-01-8; Phenanthrene	x	x	x	x	x	
ANTHRAC	120-12-7; Anthracene	x		x	x	x	
FLUORT	206-44-0; Fluoranthene	x	x	x	x	x	
PYR	129-00-0; Pyrene	x	x	x	x	x	
TRIP	217-59-4; Triphenylene	x					
B_GHI_F	203-12-3; Benzo(<i>ghi</i>)fluoranthene	x					
B_A_A	56-55-3; Benz(<i>a</i>)anthracene	x		x	x	x	
CHRY	218-01-9; Chrysene	x		x	x	x	
B_E_P	192-97-2; Benzo(<i>e</i>)pyrene	x		x	x	x	
B_B_F	205-99-2; Benzo(<i>b</i>)fluoranthene	x		x	x	x	
B_K_F	207-08-9; Benzo(<i>k</i>)fluoranthene	x		x	x	x	
D_AC_A	215-58-7; Dibenzo(<i>ac</i>)anthracene	x					
B_A_P	50-32-8; Benzo(<i>a</i>)pyrene	x		x	x	x	
D_AH_A	53-70-3; Dibenzo(<i>ah</i>)anthracene	x		x	x	x	
B_GHI_P	191-24-2; Benzo(<i>ghi</i>)perylene	x		x	x	x	
INDENO	193-39-5; Indeno(123,cd)pyrene	x		x	x	x	
ANTHAN	191-26-4; Anthanthrene	x					
RETENE	483-65-8; Retene			x	x	x	
INDENE	95-13-6; Indene		x				
CORON	191-07-1; Coronene			x	x	x	

Table II-4: Limits of detection for air and precipitation trace metal concentration measurements

Parameter	Working Recommendation ^b	MOE ^c	AES		NWRI	EPA ^{f,g}
Air Metals			ICP ^d	NAA ^e		
Pb	1 ng/m ³	0.03 ng/m ³	1.98 ng/m ³	N/A	n/a	0.074 ng/m ³
As	0.012 ng/m ³ / 0.1 ng/m ³	0.1 ng/m ³	N/A	0.13 ng/m ³	n/a	0.019 ng/m ³
Se	0.1 ng/m ³	n/a	N/A	0.39 ng/m ³	n/a	0.007 ng/m ³
Cd	0.24 ng/m ³ / 0.1 ng/m ³	0.1 ng/m ³	0.27 ng/m ³	N/a	n/a	0.103 ng/m ³
Al		0.1 ng/m ³	23.76 ng/m ³	53.85 ng/m ³	n/a	0.842 ng/m ³
Cr		n/a	1.27 ng/m ³	5.41 ng/m ³	n/a	0.018 ng/m ³
Cu		n/a	2.28 ng/m ³	21.60 ng/m ³	n/a	0.020 ng/m ³
Zn		0.2 ng/m ³	20.52 ng/m ³	2.70 ng/m ³	n/a	0.038 ng/m ³
Hg		N/A	N/A	N/A	n/a	n/a
Other Air Parameters						
TSP				2.8 µg/m ³	n/a	
TOC				2.0 µg/m ³	n/a	
PM-10					n/a	
Precipitation Metals						
Pb	--/ 0.1 ng/L	0.02 µg/L	n/a		0.2	10 ng/L
As		0.1 µg/L	n/a		0.1	20 ng/L
Se		n/a	n/a		2	100 ng/L
Cd		0.05 µg/L	n/a		0.1	7 ng/L
Al		0.05 µg/L	n/a			10 ng/L
Cr						40 ng/L
Cu						6 ng/L
Zn		0.1 µg/L	n/a			6 ng/L
Hg		N/A	n/a		N/A	N/A
Sample Volume						
Air	n/a	n/a				n/a
Precipitation	0.02 cm	0.02 cm	n/a	n/a	0.05 cm	0.02 cm

^a Limits of detection are defined in QAPP.

^b Working recommendation is the initial proposed recommendation for the DQI.

^c MOE reports W instead of LOD. W = the smallest reporting increment (2/3*σ rounded to the nearest 1, 2, or 5). Air LOD's are based on an average air volume of 80 m³. Precipitation LOD's are based on a presumed sample volume of 10 litres.

^d ICP analysis performed on one strip of the filter after a water extraction. LOD is based on a presumed sample volume of 1600 m³. ICP analysis for aluminum has a systematic bias of 50% of the NAA results.

^e NAA analysis performed on a second strip of the filter. LOD is based on a presumed sample volume of 1600 m³.

^f EPA LOD's for airborne particulate metals are based on a presumed sample volume of 96 m³.

^g EPA does not have LOD's available for precipitation samples.

N/A Not Available.

n/a Not applicable.

-- indicates no initial recommendation.

Table II-5: Additional Trace Elements Measured by Agency and Medium

Element	AES Air - NAA ^a	AES Air - ICP ^b	NWRI Precip.	EPA Air ^c	EPA Precip. ^d
B		x			
Ba		x	x		
Be		x			
Bi		x			
Br	x			x	
Ca	x		x	x	x
Ce	x				
Cl	x			x	x
Co	x		x		
Cs	x				
Fe	x	x	x	x	
Hf	x				
I	x				
In	x				
K	x		x	x	x
La	x				
Mg			x	x	x
Mn	x	x	x		
Mo		x			
Na	x		x	x	x
Ni	x		x	x	
P		x		x	
Rb	x				
S				x	
Sb	x				
Sc	x				
Si	x			x	
Sr		x	x		
Sn	x				
Ta	x				
Th	x				
Ti	x			x	
U	x				
V	x	x	x		
W	x				

^a NAA Analysis performed by Dr. Sheldon Landsberger (University of Texas - Austin)^b ICP analysis performed by Barringer MDS Laboratories (Rexdale, Ontario)^c EDXRF analysis performed at EPA Research Triangle Park (NC)^d Dionex analysis performed at Illinois State Water Survey (Champaign, IL)

II.1.2 IADN Sites

IP1 called for the establishment of one master station on each of the five Great Lakes. This was accomplished in Phase I. The station locations are listed in Table II.6.

Table II-6: IADN Master Station Locations

Lake	Site	Latitude	Longitude	Altitude (masl)	Lead Agency	Year started
Superior	Eagle Harbor	47° 27'47"	88° 08'59"	185	EPA	1990
Michigan	Sleeping Bear Dunes	44° 45'40"	86° 03'31"	241	EPA	1991
Huron	Burnt Island	45° 49'42"	82° 56'53"	180	EC	1992
Erie	Sturgeon Point	42° 41'35"	79° 03'18"	176	EPA	1991
Ontario	Pt. Petre	43° 50'34"	77° 09'13"	75	EC	1988

IP1 called for installation of eleven satellite stations by the end of Phase II and a further 11 by the end of Phase III. As discussed in Section I, installation of these stations was deferred pending a review of the initial IADN data. However, these data have shown for many of the long-range transported OCs and PCBs that there is less spatial variability than originally expected across the lakes and, therefore, a de-facto decision was made not to proceed with the installation of new IADN satellite stations. This decision was made easier since there were insufficient resources available to install and run new satellite stations in any case.

In Canada, however, there were several existing networks relevant to IADN. These included:

1. Ontario Ministry of Environment and Energy's seven station Air Toxics Network (in 1996, the MOE dropped 3 of their seven stations),
2. Environment Canada (Ontario Region), Ecosystem Health Division's eight station precipitation-only network, and,
3. Atmospheric Environment Service's pre-existing air-only station at Egbert (since

1988).

Since these other networks were linked by cooperative sampling at the Point Petre Master Station, Canada made a decision in 1995 to treat these stations as satellite facilities.

In the U.S., two additional sites which were part of the Lake Michigan Mass Balance Project were similarly included into IADN:

4. Illinois Institute of Technology in Chicago, and,
5. Brule River in Wisconsin.

The location of satellite stations operating in 1997 are shown in Table II.7. There are 14 such stations serving as satellite facilities under the program. They do not all meet the original design criteria for IADN stations in that not all sites measure all components of the programme; nor do they all conform to the siting criteria. All the sites shown in Table II.7 will be subjected to the IADN QA/QC protocols. These sites serve a valuable purpose by extending the resolution capability of IADN.

Table II-7: Satellite facilities under IADN

Lake	Station	Latitude	Longitude	Altitude (masl)	Lead Agency for Site	Measurement	Start Date
Superior	Sibley	48° 29' 48"	88° 41' 05"	215 m	EHD	Precip. organics; metals	1978
Superior	Turkey Lakes	47° 02' 05"	84° 22' 50"	380 m	"	"	1981
St. Clair	St. Clair	42° 22' 50"	82° 24' 15"	176 m	"	"	1991
Erie	Pelee Is.	41° 58' 06"	82° 31' 16"	175 m	"	"	1994
Erie	Rock Point	42° 50' 51"	79° 32' 44"	180 m	"	"	1994
Ontario (urban)	Burlington	43° 22' 36"	79° 50' 54"	200 m	"	"	1992
Ontario (urban)	Metro Zoo	43° 52' 21"	79° 11' 18"	170 m	"	"	1992
Superior	Wolf Ridge	47° 23' 00"	91° 12' 25"	344 m	MOE	All	1990
Huron	Grand Bend	43° 20' 13"	81° 44' 25"	170 m	MOE and EHD	"	1991
Huron (rural)	Dorset	45° 13' 26"	78° 55' 52"	320 m	MOE	"	1989
Erie	Port Stanley	42° 40' 22"	81° 09' 55"	213 m	"	"	1989
Huron (rural)	Egbert	44° 13' 57"	79° 46' 53"	251 m	AES	Air organics and metals	1988
Superior	Brule River	46° 44' 51"	91° 36' 30"	185 m	EPA	All	1993
Michigan (urban)	IIT-Chicago	41° 50' 04"	87° 37' 29"	199 m	EPA	All	1994

The locations of the sampling stations is shown on the map on Figure II-1.

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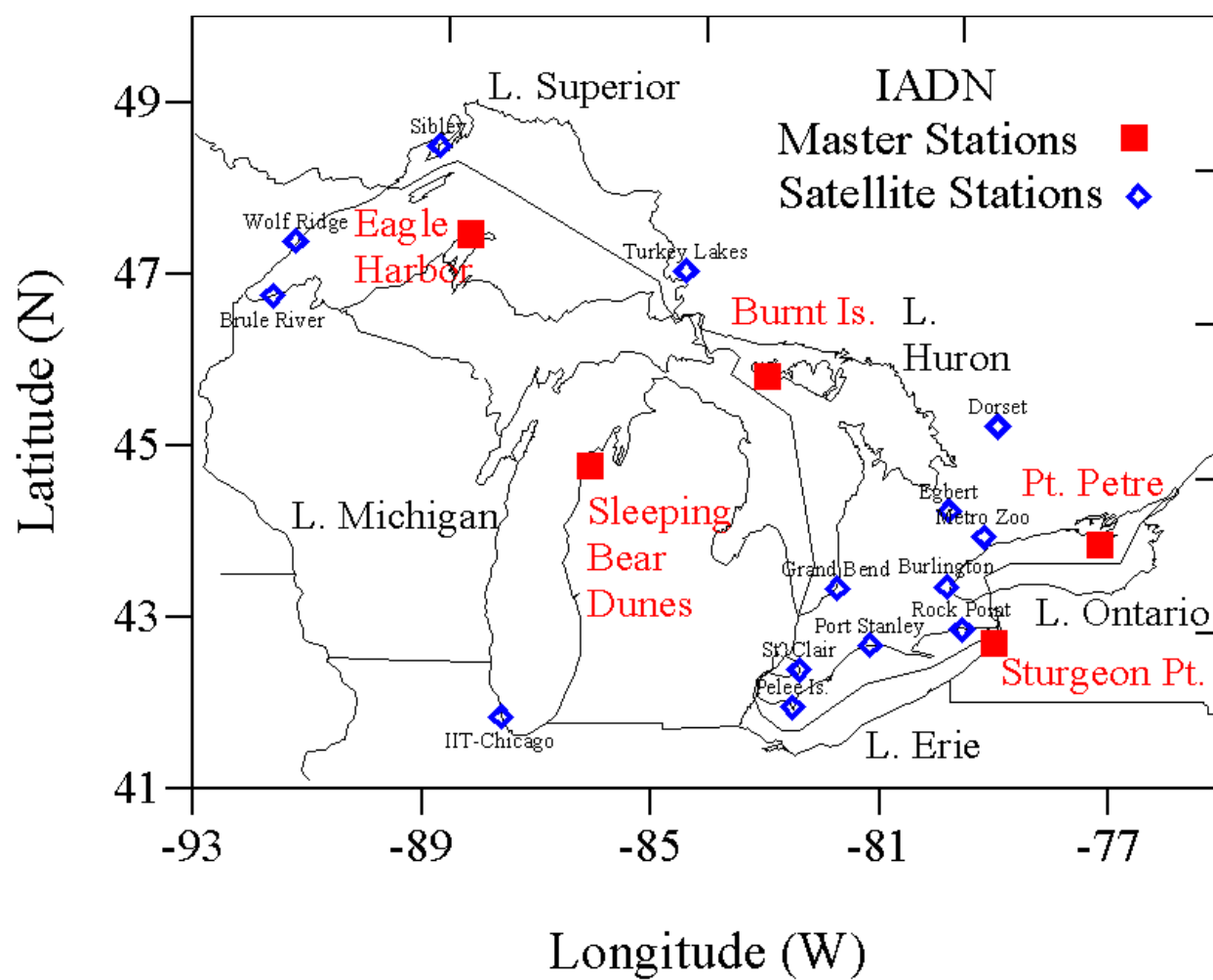


Figure II-1: Locations of current sampling stations

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II.1.3 Siting Criteria

In 1990, the IADN Operations Working Group established the siting criteria for IADN. These siting criteria are given in Appendix D of the IADN Quality Assurance Program Plan (QAPP). Nine siting criteria were selected:

1. Sites should be regionally representative (within 1 km of the sites land use should represent the surrounding area out to 40km). Satellite sites may deviate more from this criterion.
2. Sites should be >40km from population areas of >10000 inhabitants, heavy industry, or other major sources of air pollutants.
3. Sites should be >10km from other important sources (population 1000-10000), mining, manufacturing facilities, major highways, commercial areas, electrical transfer stations or sources ten times smaller than those in criterion 2.
4. Sites should be >1km from local sources, such as boat traffic (>30 vehicles/hr), farms or tilled fields, fuel or storage areas, landfills, sewage lagoons or small towns (<1000). Where pesticides are used within the 1 km radius, their use should be documented.
5. Sites should be >250m from single residences, parking lots, grazing animals, public roads. Where residences are 250-1000m from the site, they should be outside of a 22.5° sector on either side of the prevailing wind.
6. Samplers should be on level terrain (slope <15%) with regionally representative ground cover. Samplers should subtend a vertical angle of less than 30° with any obstruction (trees, towers, power lines). In areas of high snowfall, the site should be sheltered by trees at a distance of 2.5 to 4 times their height. Samplers should be on 1 m platforms.
7. Sites should be no more than 1 km from the lake shore. Sites should preferentially be placed so that prevailing winds are off the lake.
8. Sites should have all weather access, sufficient electrical power and a security fence. 2m spacing between samplers is desired.
9. No development within 1 km of the site is planned, and the site should be viable for at least 5 years.

For the Master Stations, only Sturgeon Point does not meet all of these siting criteria, failing criteria 2. Sturgeon Point is 22 kilometers west of Buffalo, NY. Finding a site for Lake Erie site proved to be difficult because considerable development exists all along the Lake Erie shorefront. Sturgeon Point was the best compromise site for the U.S. side of Lake Erie.

II.1.4 Sampling/Analysis Protocols - Methods Development

IADN Master Stations all contain the required elements of the IP1 sampling design. The details of such sampling protocols are given in the Sampling Procedures Manuals for each agency. These details will be reviewed briefly here and shown in Table II.8. All stations (including all satellite facilities except Egbert) contain samplers to measure wet deposition of gaseous organics. The sampler used for the organics measurements is uniform across the network, an MIC-B collector with stainless steel funnel. EPA/Indiana University, MOE and NWRI all use XAD-2 resin column cartridges for capturing the organics. EHD uses a dichloromethane solvent extraction system in which the rainwater is bubbled through a 250 ml dichloromethane volume. EPA/Indiana University, MOE and NWRI sample on a 28-day cumulative basis, EHD takes a 14d cumulative sample. Although EHD has twice as many samples as the other agencies, the start and finish dates for the 28-day period are aligned among all agencies. Trace metals in precipitation measurements vary between agencies. MOE uses a long polypropylene tube on an MIC collector, while NWRI uses a traditional MIC with inorganic ion precipitation bags (CAPMoN) which are subsequently acid leached before the sample is removed from the bag. Both agencies employ a 28-day cumulative precipitation collection cycle.

Organics air sampling is made using high volume samplers with filter and absorbent combinations. EPA/Indiana University and MOE use a HiVol of identical design which has an XAD absorbent cartridge. This allows gathering over 2000 m³ of sample volume. AES uses polyurethane foam as the absorbent for organics. Sample volumes are kept below 400 m² to avoid breakthrough of lighter organics during warm summer months. All agencies have now adopted a sampling frequency of a 24-hour

composite every 12 days. Due to the low analyte masses on the filters, agency protocols have changed over the course of the IP1 period. Early results showed that little organochlorine mass was found on the filter. Table II-12 (below) will show that, at the Point Petre station in 1992, the particulate/gaseous mass ratio is 2.3% for Σ PCBs, <1% for the HCHs, pp,DDE, and HCB, and 43% for p,p'-DDD and 53% for p,p'-DDT. p,p'-DDD ranged from 3-70% particulate at the US sites over the years 1992-1994 and p,p'-DDT ranged from 7-25% particulate at these sites. This limited additional data for the OCs from filter measurements led Environment Canada to terminate the measurements of OCs on filters in 1993 and the EPA followed suit in 1995. MOE combines the gas and particulate fractions to arrive at a total concentration for OCs and PAHs.

Table II-8: Summary of sampling and analysis methods

Media/Parameter	Agency	Sampling Method ^a	Sampling Frequency ^b	Analytical Method	Reporting Units
Air Organics (PCBs, Pesticides, PAHs)	AES	HiVol PUF Sampler: GFF + PUF	24 hr/12 days	Soxhlet/GC-ECD (PCBs, Pesticides); HPLC-fluorescence (PAHs)	pg/m ³
	MOE	HiVol: GFF + XAD16	24 hr/12 days	Soxhlet/GC-ECD or GC/MS	ng/m ³
	Indiana U	HiVol: GFF + XAD2	24 hr/12 days	Soxhlet/GC-ECD (PCBs, Pesticides); GC/MS (PAHs)	pg/m ³
Air Metals	AES	PM10/15 HiVol	24 hr/12 days	ICP-MS or INAA	ng/m ³
	MOE	LoVol	28 days	ICP	ug/m ³
	EPA	PM10 Dichot	96 hr/28 days	XRF	ng/m ³
Precipitation Organics (PCBs, Pesticides, PAHs)	NWRI	MIC-B/XAD2	28 days	GC-ECD	ng/L
	EHD	MIC-B/DCM	14 days	GC-ECD or GC-ECD-MS	ng/L
	MOE	MIC-B/XAD16+ GFF	28 days	GC-MS	ng/L
	Indiana U	MIC-B/XAD2	28 days	GC-ECD	ng/L
Precipitation Metals	NWRI	MIC-AU	28 days	ICP, AAS	ug/L
	EHD	MIC-A	monthly	ICP	ug/L
	MOE	MIC-A	28 days	ICP-MS	ug/L
Related Air Measurements					
Total Organic Carbon	AES	HiVol/GFF	24 hr/6 days	Thermal Desorption	ug/m ³
Total Suspended Part.	AES, Indiana U	HiVol/GFF	24 hr/6 days	Gravimetric	ug/m ³
PM10	Indiana U	Dichot/TF	96 hr/mo.	Gravimetric	ug/m ³
Meteorology ^c					
Temperature	AES, Indiana U, MOE	Thermistor	hrly. avg.	Direct Reading	°C
Relative Humidity	AES, Indiana U, MOE	Hygristor	hrly. avg.	Direct Reading	Percent
Barometric Pressure	Indiana U		hrly. avg.	Direct Reading	kPa
Wind Speed	AES, Indiana U, MOE	Anemometer	hrly. avg.	Direct Reading	m/s
Wind Direction	AES, Indiana U, MOE	Vane	hrly. avg.	Direct Reading	Degrees
Precipitation Amount	AES, MOE	Type B Rain Gauge	24 hrs	Direct Reading	mm
	Indiana U, AES	Belfort gauge	continuous	Direct Reading	mm
Solar Irradiation	AES, MOE	Pyranometer	hrly. avg.	Direct Reading	w/m ²
	Indiana U	Pyranometer	hrly. avg.	Direct Reading	Langleys

NOTES:

- ^a Sampling and analysis methods used by different groups may appear similar, but differ significantly in operational and other details.
- ^b Sampling frequency is sometimes given as sample duration/sampling interval.
- ^c MOE operates meteorological equipment at their Dorset station only.

KEY TO ABBREVIATIONS

AAS atomic absorption spectroscopy
 DCM dichloromethane solvent
 Dichot dichotomous sampler
 ECD electron capture detector
 GC gas chromatography
 GFF glass fibre filter
 HiVol high volume sampler
 ICP inductively coupled plasma spectrometry

INAA instrumental neutron activation analysis

LoVol low volume sampler
 MIC-A MIC type A precipitation sampler
 MIC-AU MIC type AU precipitation sampler
 MIC-B MIC type B precipitation sampler
 MS mass spectrometry
 PM10 particulate matter less than 10µm in diameter
 PUF polyurethane foam plug
 XAD XAD resin
 XRF x-ray fluorescence

AES dropped the particulate organochlorine analysis after 1991 and retained the high

time resolution (1 day in 6 up to 1994 and 1 day in 12 thereafter) for the PAHs in order to better determine potential source information (see section II.4.2). In the United States, both gas and particulate fractions are analyzed for organochlorines and PAHs, however, EPA has suggested that their laboratory also forego the particulate organochlorine analyses. This decision is supported by analysis of the loadings results obtained so far (see section II.3).

Laboratory analysis protocols generally call for solvent extraction of the organic sampling media, nitrogen blowdown to small volume (typically 1µl) and injection on GC-ECD or GC-MS. Details of these analyses can be found in the Laboratory Protocol Manuals or the agency project plans (QAPjPs). Variations in columns and GC programming leads to different chromatography between agencies. Thus, in Table II-2, one finds that the PCB congeners reported by various laboratories may not identically match (some laboratories resolve certain congeners, other laboratories have congener overlap). There is a need to standardize the reporting of the PCBs between agencies and a suggestion was made in 1994 (Hoff and Sweet, 1994) that a suite of well resolved PCB congeners be used to define the PCB concentrations. This has yet to be adopted since there is a large degree of inertia to continue to report Σ PCB as a variable. It is expected that resolution of the issue of what PCBs need be measured and how to report them will need to happen during the second IADN Implementation phase.

The three agencies involved in measuring trace metals in air utilize different sampling equipment and sampling frequencies, as shown in Table II-8. AES uses a HiVol sampler, MOE uses a LoVol sampler, and EPA's contractor uses a Dichotomous sampler. There is a need to harmonize sampling frequencies, as AES collects a 24-hour composite sample every 12 days, MOE collects a 28-day composite sample, while EPA collects a 96-hour composite sample every 28 days.

The Point Petre and Eagle Harbor Master Stations both contained replicated sampling for air and precipitation organics until the end of Phase I. At that time, a replication study (Hoff and Brice, 1993) showed that the coefficient of variation between the three AES colocated air samplers was 31.4% for PCB 16/32, 13.3% for α -HCH, 15.4% for γ -HCH, 11.5% for trans-chlordane, 22.0% for B(k)F and 13.9% for B(a)P.

These results were consistent at Illinois State Water Survey, Ontario Ministry of Environment and Energy and Atmospheric Environment Service sampling sites, where replication studies were also occurring. Because of this reproducibility in measurements and due to resource pressures, it was decided that continuous replication studies were no longer necessary at the Point Petre Master Station for all measurements. Replication of precipitation measurements for organics continues to the present in the NWRI sampling protocol. Data for the target analytes in precipitation are more variable than is the case for air samples and the replication provided for this medium at Point Petre allows some assessment of the uncertainties associated with these concentrations. During 1994, EHD installed three organic precipitation samplers at the IADN satellite station in Burlington, to determine the total (field and laboratory) variability in deposition estimates at a given site. Deposition estimates from the three samplers showed variability of <10% for the organochlorine pesticides, and 24% for total PCBs. Statistical analysis of the data showed that, at the 95% level, there were no significant differences in results from the three samplers. At the U.S. sites, a protocol of rotating replication between air samplers is used where one duplicate sample per month is obtained from one of the three sites.

Metals analysis is conducted using NAA and ICP in Canada for particulates, EDXRF in the US for particulates, and ICP-MS and GFAAS for precipitation analyses. It is expected that mercury will be integrated into the IADN suite of chemicals during the next implementation period.

Additional information from the use of a total suspended particulate (TSP) sampler and a total organic carbon (TOC) sampler has not been as useful as originally intended. The main use of these two parameters is in the apportionment of material between the gaseous and particulate phases (Yamasaki et al., 1982; Pankow, 1987). TSP is a surrogate for particulate surface area in these theoretical calculations and it was hoped that TOC would provide a better scaling parameter than TSP. In practice, however, the TOC/TSP ratio has been remarkably well defined ranging from 0.11 ± 0.09 at the three Canadian sites. It can be concluded that with such a low variability in this parameter, TSP/TOC analysis should be discontinued. A second factor which has arisen is that new continuous monitors (TEOMs, R&P Inc., Rochester, NY) have become available to give

real-time measurements of PM_{2.5} and PM₁₀ and are now acceptable as EPA methods for particulate mass. The use of these continuous monitors will be preferable to the gravimetric filter analysis used previously.

Over the course of the IP1 period, considerable method development has been carried out in order to add new chemicals to the IADN list. Epithermal NAA techniques were modified to improve the analyte list for particulate metals on the Canadian side (Biegalski, 1996). Methods to reliably analyse co-planar PCBs using multidimensional GC (Brice et al., 1996a) and toxaphene (Brice et al., 1996b; Shoeib et al., 1997) are in development. Application of HPLC fluorescence detection techniques (Alexandrou et al., 1997) have been reported. Field methods to include gaseous and particulate mercury in the network are currently being tested (Lu and Schroeder, 1997). The use of enantiomeric ratios of certain pesticides have given potentially important results as a tracer of organochlorine sources (Ridal et al., 1996b). Methods to understand the particulate size distribution of PAHs have been tested and reported (Poster et al., 1995). Use of short term sampling techniques have been employed to study diurnal variations in PCBs and endosulphan (Wallace and Hites, 1995, 1996b). In addition, laboratory methods have been examined to determine whether air inside laboratories themselves are sufficiently clean to make proper PCB measurements (Wallace and Hites, 1996a).

II.1.5 Quality Assurance/Quality Control

IP1 called for the production of Quality Assurance Program Plans (QAPPs), Project Plans (QAPjPs) and Standard Protocol Manuals (SPM). These have all been produced.

The IADN QAPP was signed by Program Management on February 28, 1994. The AES QAPjP was signed on February 11, 1994.

A Sampling Procedures Manual for Environment Canada was produced in 1990 and revised in 1994 (Environment Canada, 1994). USEPA, through its contractor Illinois State Water Survey, released its first version of their manual in 1990. The new contractor, Indiana University, has published a SPM (Basu, 1995).

The QA/QC program development was a major achievement during the program startup. The IADN QAPP and the SPMs have been consulted as models in other

atmospheric toxics monitoring efforts, such as the Environment Canada St. Lawrence Action Plan, the Indian and Northern Affairs Canada Northern Contaminants Program, the Environment Canada Environmental Monitoring and Assessment Program, and the UN Economic Commission for Europe Monitoring and Evaluation Project (EMEP). A notable success of IP1 was the QA/QC investigations on interlaboratory intercomparability. During 1992-1994, nine round robin studies were carried out (Cussion, 1992a; Cussion, 1992b; Cussion, 1992c; Cussion, 1992d; Cussion, 1994a; Cussion, 1994b; Cussion, 1996a, Cussion, 1996b; Cussion, 1996c). [Note that these studies were conducted while Illinois State Water Survey was the US contractor, and don't reflect the performance of Indiana University.] These studies all applied to both precipitation and air analyses, and covered a range of concentrations. The first four round-robins focused on analysis of injection-ready standards for PCBs, PAHs, OCs and trace metals; the next four studies included the clean-up steps. Only Study 94-1 (Cussion, 1996c) specifically looked at matrix samples for air and precipitation. These studies showed:

- Interlaboratory means and medians of PCB isomers for three or more chlorine atoms agreed, but relative standard deviations between laboratories were frequently >20% which required exchange of standards (Cussion, Study 92-1, 1992)
- For the first PAH round robin, the six laboratories had analyses within 75-110% of the target compounds for 71, 56, 81, 40, 62, and 52% of the samples. There were few systematic biases noted. Sources of variability indicated the need to use different solvents for analyses (Cussion, Study 92-2, 1992)
- For the first organochlorine pesticide study, agreement to better than 20% was seen for most labs. Within a laboratory, agreement with high and low concentration solutions was better than interlaboratory agreement, which could have up to 40% variability. It was felt that common reference standards could reduce this bias to less than 10-15% (Cussion, Study 92-3, 1992).

- For the trace metals standards study, all labs had agreement to better than 10% except for aluminum which was at the 30% variation level. Between participant bias was better than 20% (Cussion, Study 92-4, 1992).
- For the second OC study (injection ready solutions) better than 15% agreement was seen between laboratories and considerable improvement was seen over the first round robin study (Cussion, Study 93-2, 1993).
- For the second PCB study, results were similar to the first study with $\pm 15\%$ variability within a laboratory for most of the PCB isomers and up to $\pm 30\%$ variability for a few isomers. Between laboratory variability was in the range 20-40%. Calibration differences seem to be the main discrepancy between labs. Two labs had less than 50% of their samples within 75-110% of the target which was a concern. This may have been due to loss of some isomers (Cussion, Study 93-3, 1993).
- The second PAH study lowered the analyte concentrations to the $\mu\text{g/mL}$ level, a level at which only one laboratory was capable during the first study. This round robin had means and medians within $\pm 15\%$ of the target for almost all the parameters at this level, but the interlaboratory RSD was greater than 20% for almost all the analytes (Cussion, Study 93-4, 1993).
- Study 94-1, which included trace metals spiked into bulk precipitation, and trace metals spiked onto the filters used for air sampling, concluded that further method improvement was required in order to achieve lower detection limits. Interlaboratory comparisons for precipitation trace metal measurements were improved, relative to earlier studies, with the exception of selenium. Some labs reported quantifiable levels of trace metals on the filter blanks, which may have been due to handling and shipping. It was recommended that comparison with reference standards become standard protocol (Cussion Study 94-1, 1996).

While the interlaboratory differences may seem large in comparison to inorganic analyses, some perspective is needed for organics analyses. The trace levels at which many of these compounds occur in the environment makes their detection difficult and their precise quantitation harder. In 1994, Hoff addressed the precision required to make estimates of loadings to the Great Lakes (Hoff, 1994). This research was carried out as part of the method development effort under IADN. It was designed to assess the relative effort required under various areas of the program and provide guidance for where resources should be placed in the future. A significant conclusion was, for almost all species measured by IADN, laboratory analytical errors are a small portion of the total loading error budget. The main uncertainty in loading estimates comes from other parameters such as the particle deposition velocity, Henry's law constant, mass-transfer coefficients, etc. Some of these parameters have large (>100%) uncertainties, and for most of the species monitored in IADN, considerable improvement to the understanding of exchange would have to occur before the levels of uncertainty seen in the laboratory round-robins became a dominating concern. In fact, the laboratory precision improved faster than the knowledge of the air-water exchange processes. For this reason, research efforts, parallel to IADN, into air-water exchange were accelerated.

The main recommendations that resulted from the interlaboratory studies were:

1. All participating laboratories must use common reference standards for all classes of compounds.
2. A common target list must be agreed upon for PCB congeners and PAHs; this would considerably reduce misidentification of peaks.
3. Once the PAH target list has been decided, the type of instrument used for analysis must be specified: HPLC is preferable to GC if analysing for PAHs with more than 24 carbon atoms, however the GC has greater resolving power for smaller PAHs (i.e., less than 24 carbon atoms).

The use of QA/QC audits and new QA/QC procedures, such as the Research Data Management and Quality Assurance System (RDMQ), have provided assurance that high quality data are coming out of the IADN program, even though only limited tracking by audit staff is available. Station audits have continued at the Canadian Master Stations on

a quarterly basis throughout the program and these ensure that on-site contractors maintain protocols.

II.1.6 Data Status

Table II.9 below shows the status of the data at the time of writing this report. The codes in the table correspond to whether the samples have been taken (T), analysed(A), data reported as flat spreadsheet files (D) or put through RDMQ (R).

II.2 Temporal Trends of Organochlorines Near the Great Lakes

II.2.1 Gas-Phase Concentrations

One goal of the Integrated Atmospheric Deposition Network (IADN) is long-term monitoring and research to determine temporal trends of these persistent toxic substances. While atmospheric concentrations of compounds such as polychlorinated biphenyls (PCBs) have been studied on a relatively long-term basis by several groups (Manchester-Neesvig and Andren, 1989; Hermanson and Hites, 1989; Baker and Eisenreich, 1990; Hoff et al., 1992a,b; Panshin and Hites, 1994,a,b; Monosmith and Hermanson, 1996), none of these studies were carried out long enough to observe long-term trends. IADN was meant to rectify this deficiency. As much as six years data exist for some IADN sampling stations, providing an unique opportunity to investigate temporal trends in atmospheric gas-phase concentrations of organochlorine compounds near the Great Lakes. This section reports studies (Hillery et al., 1997; Cortes et al., 1997) which explore the temporal behavior of selected persistent organochlorine contaminants: total PCBs, DDT, hexachlorocyclohexane (HCH) isomers, hexachlorobenzene (HCB), chlordane isomers, *trans*-nonachlor, and dieldrin.

II.2.1.1 *Temperature Effects*

The determination of trends in the air concentration of gas phase organic species is complicated by a highly variable seasonal component to the concentrations, varying by over an order of magnitude for some chemicals. Fluctuations in ambient temperature are largely responsible for seasonal trends in the gas-phase concentrations. This is

demonstrated for Eagle Harbor PCB concentrations shown in Figure II-2, where concentrations are plotted versus time, along with the appropriate atmospheric temperatures for comparison. Increases in concentrations correspond to approximately

Table II-8. Current data status by agency

Compounds/Agency	ISWS/IU		AES		NWRI		EHD		MOE	
	Air	Precip	Air	Precip	Air	Precip	Air	Precip	Air	Precip
PCB										
1989	-	-	T	-	-	-	D	D		
1990	-	-	A	-	-	R ²	D	D		
1991	D	D	A	D	-	R ²	D	D		
1992	D	D	A	D	-	R ²	D	D		
1993	D	D	R ¹	D	-	R ²	D	D		
1994	D	D	R ¹	D	-	R ²	D	D		
1995	D	D	A	T	-	A	A	A		
1996	A	A	A	T	-	A	A	A		
1997	A ¹	A ¹	T	T	-	T	A ²	A ²		
OC										
1989	-	-	T	-	-	D	D	D		
1990	-	-	A	-	-	R ²	D	D		
1991	D	D	A	D	-	R ²	D	D		
1992	D	D	A	D	-	R ²	D	D		
1993	D	D	R ¹	D	-	R ²	D	D		
1994	D	D	R ¹	D	-	R ²	D	D		
1995	D	D	A	T	-	A	A	A		
1996	A	A	A	T	-	A	A	A		
1997	A ¹	A ¹	T	T	-	T	A ²	A ²		
PAH										
1989	-	-	T	-	-	D	D	D		
1990	-	-	R	-	-	R ²	D	D		
1991	D	D	R	-	-	R ²	D	D		
1992	D	D	R	-	-	R ²	D	D		
1993	D	D	R	-	-	R ²	D	D		
1994	D	D	R	-	-	R ²	D	D		
1995	D	D	R	T	-	A	A	A		
1996	A	A	A	T	-	A	A	A		
1997	A ¹	A ¹	T	T	-	T	A ²	A ²		
METALS										
1988	-	-	R	-	-	D	D	D		
1989	-	-	R	-	-	D	D	D		
1990	-	-	R	-	-	D	D	D		
1991	D	D	R	D	-	D	D	D		
1992	D	D	R	D	-	D	D	D		
1993	D	D	R	D	-	D	D	D		
1994	D	-	R	D	-	D	D	D		
1995	T	-	R	T	-	D	A	A		
1996	T	-	A	T	-	T	A	A		
1997	T	-	T	T	-	T	A ²	A ²		

T = Samples taken

A = Samples Analyzed

A¹ = Analyzed to Aug. '97

A² = Analyzed to June '97

A³ = Analyzed to

D = Data available in Flat Files/Reports

R = Data through RDMQ

**R¹ = Preliminary data delivered, some components
under review by lab.**

R² = Point Petre and Burnt Island sites

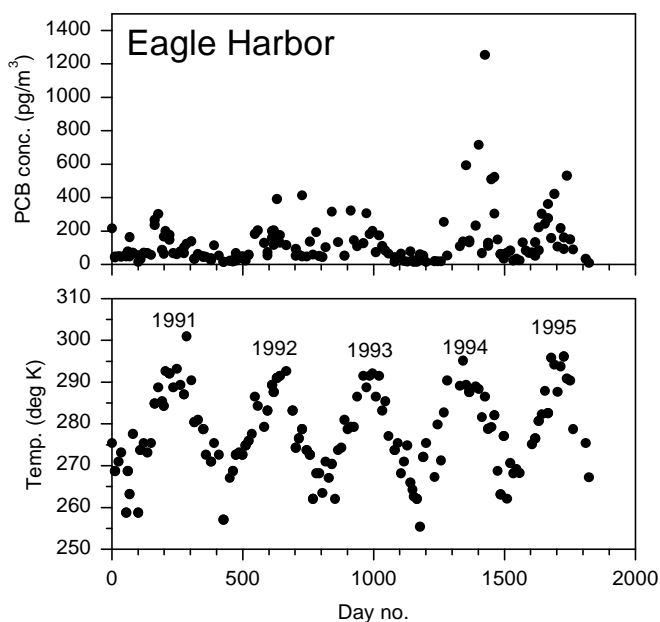


Figure II-2: Fluctuation in the gas-phase concentrations of total PCBs over time (top) and the daily mean atmospheric temperature for Eagle Harbor on Lake Superior.

June 1991, July 1992, August 1993, August 1994, and July 1995. Clearly, concentrations are cyclic and increase in the warmer summer months.

Thermodynamically, the gas-phase behavior of semi-volatile organic compounds (SVOCs) is described by the Clausius-Clapeyron equation:

$$\ln(P) = \left(\frac{-\Delta H_{vap}}{R} \right) \left(\frac{1}{T} \right) + const$$

Equation II-1: Clausius-Clapeyron Equation

where P is the partial pressure in atmospheres, T is the temperature in °K, ΔH_{vap} is the heat of vaporization in J mol⁻¹, and R is the gas constant. Clausius-Clapeyron plots were developed for

each compound in this study to further examine the temperature dependence of atmospheric SVOC concentrations. An example is given in Figure II-3 for PCBs at the three U.S. sites. Each graph in Figure II-3 shows the natural logarithm of the partial pressure for total PCBs (based on the summation of the partial pressures of individual congeners) versus the reciprocal of the average atmospheric temperature for the appropriate 24 hour sampling period. These data cover the period from inception of sampling at each site to November 1995.

Clearly, PCB partial pressures increase with temperature. A regression applied to these data gives a linear relationship, with correlation coefficients which are all significant at the 99% confidence level or higher. ΔH_{vap} , calculated from the slopes of the regression lines, are 37 kJ mol⁻¹ at Eagle Harbor, 37 kJ mol⁻¹ at Sleeping Bear Dunes, and 38 kJ mol⁻¹ at Sturgeon Point. These values are consistent with one another, but they are about half the previously reported heats of vaporization for PCBs (Hinckley et al., 1990; Hoff et al., 1992b; Panshin and Hites, 1994a; Falconer and Bidleman, 1994). A significant negative slope was also found for plots of $\ln P$ versus $1/T$ for all of the pesticides in this study, indicating that gas-phase concentrations increase with increasing temperature. These slopes, when converted to ΔH_{vap} , are also about half of the expected values. There are a number of reasons why the Clausius-Clapeyron slopes are less than literature values, but work in progress will suggest that it is due to a combination of volatilization from varied surface types (soil, water, vegetation) and long-range transport (Hoff et al., 1997).

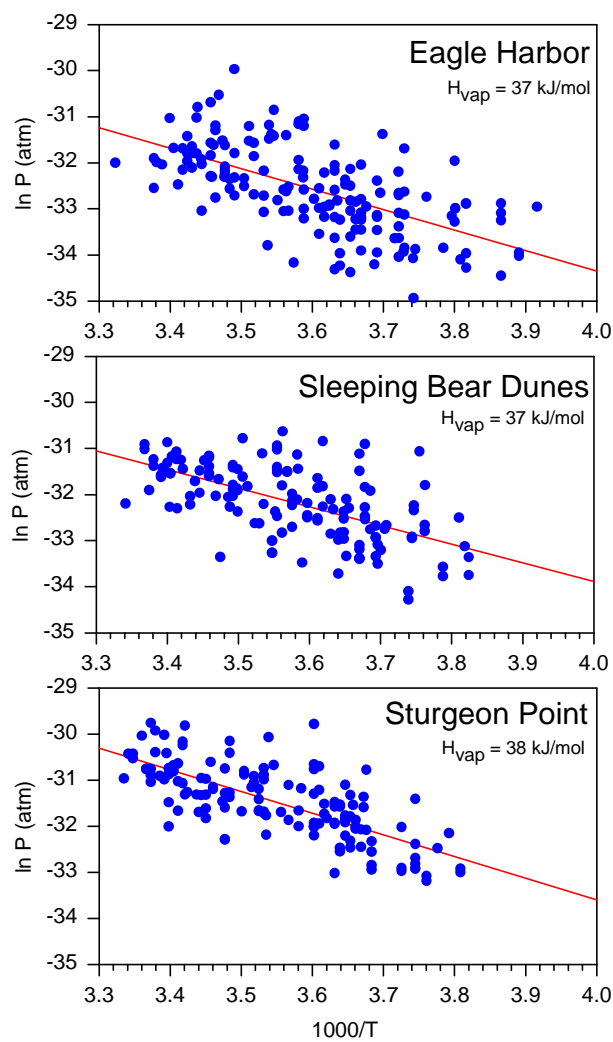


Figure II-3: Clausius-Clapeyron plots relating the natural logarithm of the partial pressure of total PCBs to the inverse temperature (in Kelvin), at three of the IADN Master Stations.

II.2.1.2 Temporal Trends in PCBs

Starting with the relationship between the natural logarithm of the partial pressure and the inverse temperature, time was added (as relative Julian day) as a parameter and a multiple linear regression using equation II.2 was performed:

$$\ln(P) = a_0 + a_1 \left(\frac{1}{T} \right) + a_2 \text{ time}$$

Equation II-2: Time-temperature trend regression

Notice that $-a_2$ is a first-order rate constant. Temperature is still the predominant parameter, but the coefficients for the time term are interesting. For Eagle Harbor, this term is $0.000007 \text{ day}^{-1}$ and has a standard deviation of about $\pm 1600\%$; however, the standard deviation for this term at Sleeping Bear Dunes is $\pm 37\%$, and at Sturgeon Point it is $\pm 41\%$. At both Sleeping Bear Dunes and Sturgeon Point, the time coefficients are about the same and negative ($-0.00033 \text{ day}^{-1}$ and $-0.00027 \text{ day}^{-1}$, respectively), indicating a decline in partial pressures over time. To ensure that this result was not an artifact of including the 1991 data only for Eagle Harbor, the regression was repeated using only values from 1992 onward. To ensure that the results were not an artifact of switching from PUF to XAD resin for the sample collection, the regression was repeated for all sites using only data from May 1992 onward. In both cases, there were slight differences in the numbers obtained, but no differences in the trends. Therefore, results are presented using the entire data set. It should be noted that the lack of a clear trend for Lake Superior is consistent with the known slow change in the concentration of other chemicals, such as toxaphene (Pearson et al., 1997). Reasons given for those slow changes are the coldness of the lake, its low particulate content and, therefore, in relation to Lakes Erie and Ontario, slow removal processes of the chemical from the water column. The air concentrations over the lake reflect this slow decrease in water concentrations.

Based on an average rate constant of 0.0003 day^{-1} , the environmental half-life of PCBs in the atmosphere near Lake Michigan and Lake Erie is about 6 years. This differs considerably from previously reported atmospheric PCB data; see Table II.10. Panshin and Hites (1994b) sampled air in Bloomington (Indiana) in 1993 and compared the results to the 1986-87 study of Hermanson and Hites (1989). They found no evidence that atmospheric concentrations were changing. Panshin and Hites (1994a) also sampled air coming in off the ocean to Bermuda. These results were compared to 20 years of literature data, and again no decline in atmospheric

PCB concentrations could be detected. These later experiments focused on background atmospheric PCB levels, and these authors avoided any local influence by sampling only when the wind was blowing over the open ocean. Thus, the situation in Bermuda may be similar to the situation at Eagle Harbor, where there is no statistically significant trend in the atmospheric PCB levels. In addition, this result is similar to that of Baker and Eisenreich (1990), who reported that atmospheric PCB concentrations over Lake Superior remained relatively constant during a 10 year period.

Atmospheric half-lives in this study refer to the time it takes for the concentration of a specific compound at a specific location (sampling site) to decrease by 50% according to observations made by this study. This half-life is a function of many chemical, physical, and

Table II-9: The Half-lives of PCBs in Various Environmental Compartments

Compartment	Half-life (years)	Reference
Air, Lake Superior	no change (in 10 years)	Baker & Eisenreich (1990)
Air, Bermuda	no change (in 23 years)	Panshin & Hites (1994a)
Air, Bloomington	no change (in 7 years)	Panshin & Hites (1994b)
Water, Lake Superior	2.5-6.3	Jeremiason <i>et al.</i> (1994)
Water, Lake Michigan	9	Pearson <i>et al.</i> (1996)
Vegetation, U.K.	4	Jones <i>et al.</i> (1992)
Moss, Norway	6-14	Lead <i>et al.</i> (1996)
Soil, U.K.	3-17	Alcock <i>et al.</i> (1993)
Mussels, Mediterranean	9	Sole <i>et al.</i> (1994)
Bloaters, Lake Michigan	8	Hesselberg <i>et al.</i> (1990)
Trout, Lake Michigan	4	Devault <i>et al.</i> (1988)
Trout, Lake Michigan	6.3	Miller <i>et al.</i> (1992)
Trout, Lake Ontario	10	Borgmann & Whittle (28)
Pike, Baltic Sea	9	Moilanen <i>et al.</i> (1982)
Spot-tail shiners, Great Lakes	5	Suns <i>et al.</i> (1993)
Fish, Lake Michigan	7	Stow (1995)
Gull eggs, Lake Ontario	6	Irwin & Lageroos (1988)
Gull eggs, Lake Erie	no change (in 10 years)	Irwin & Lageroos (1988)
Gull eggs, Lake Superior	18	Smith (1995)
Gull eggs, Lake Ontario	21	Smith (1995)
Arctic ringed seals	6	Addison <i>et al.</i> (1986)
Arctic polar bears	15	Norstrom <i>et al.</i> (1988)

meteorological processes operating at geographically diverse source locations. The relative contributions of these phenomena are site specific. This atmospheric half-life should not be taken to be the half-life attributable to any one degradation process in a generic environment.

The half-life of about 6 years for atmospheric PCBs at Sleeping Bear Dunes and Sturgeon Point compares favorably with trends observed in other environmental compartments; see Table II.10. PCBs have been declining in water with half-lives of 3-9 years (Jeriamiason et al., 1994; Pearson et al., 1996). A half-life of 4 years can be estimated for PCB concentrations in vegetation (Jones et al., 1992), 6-14 years for moss (Lead et al., 1996), and 3-17 years for soil (Alcock et al., 1993). PCBs in mussels in Fangar Bay in the western Mediterranean declined with a half-life of about 9 years, though mussels in another area (Alfacs Bay) of the region showed no decline (Sole et al., 1994). The average half-life of PCBs in fish is about 7 years (Hesselberg et al., 1990; DeVault et al., 1988; Miller et al., 1992; Borgmann and Whittle, 1991; Moilanen et al., 1982; Suns et al., 1993; Stow, 1995), but in gull eggs, it seems to vary from about 6 to over 25 years (Irwin and Lageroos, 1988; Smith, 1995). For both fish and gull eggs, determining temporal trends in PCBs is complicated by internal lake processes such as changes in prey dynamics (Smith, 1995). Stow (1995) looked at 20 years of PCB concentrations from fish in Lake Michigan, applying corrections for the effects of species, location, and size. Estimates from these data for 1978 to 1992 gave a half-life of about 7 years. The half-life of PCBs in Arctic ringed seals (Addison et al., 1986) is about 6 years, and in polar bears (Norstrom et al., 1988) it is about 15 years. This latter value may be higher due to the paucity of data available for analysis of temporal trends, or it may be attributable to the higher trophic level of polar bears.

In contrast to these clear changes in the water and biota PCB concentrations, the lack of any observable trend (until now) in the atmospheric PCB concentrations was peculiar. It now seems likely that long-term changes are hidden by large seasonal (temperature) effects. In addition, most long-term comparisons were based on data obtained by different researchers,

using different analytical methods and different time periods, making direct comparisons inconclusive. This problem was one of the reasons for the creation of IADN.

II.2.1.3 *Temporal Trends in Pesticides*

The parameters in equation II.2 were also estimated for ten pesticides at all five IADN sites. Nearly all of the coefficients of temperature (a_1) were statistically significant at the 99.99% confidence level, and about 70% of the coefficients of time (a_2) were statistically significant at the 95% confidence level. Data at Burnt Island does not show any significant temporal trends, probably because there were only three years of data at this site for this analysis. For this reason, the Burnt Island data will not be discussed further here. Temperature and time were found to explain more than 50% of the variance (measured as r^2) for over half of the pesticide/site combinations.

For the pesticides, nearly all of the coefficients determined for the time term in equation II.2 are negative and of about the same magnitude. This indicates that the partial pressures of these compounds are decreasing at about the same rate. The environmental atmospheric half-life for each compound at each site is shown in Table II.11. The decreasing trend is significant for the HCH and DDT related compounds at most sites, the exception being DDT at Point Petre. At the sites where the half-lives of DDT are significant, they are also similar, about 3 years. DDE, the primary metabolite of DDT, is not declining as rapidly at Eagle Harbor, Sturgeon Point, or Point Petre, where half-lives are 5, 7, and 9 years, respectively. The HCH isomers are decreasing with a half-life of 5 years or less, except for γ -HCH at Point Petre, where the half-life is 7 years. It is important to note that γ -HCH has been used during summer months in Ontario (Hoff et al., 1992b), and in fact γ -HCH shows a strong seasonal cycle not accounted for by temperature. This is not the case for the other pesticides in this study. The half-life of HCB is longer than that of the HCH isomers at all sites, ranging from 3 years at Sleeping Bear Dunes to 12 years at Eagle Harbor, the longest significant half-life determined from this data. The temporal parameters for the chlordane compounds are significant at Sleeping Bear Dunes, Sturgeon Point, and Point

Petre, with half-lives ranging from 3 years for γ -chlordane to 9 for *t*-nonachlor. Dieldrin was found to be decreasing at all sites, with half-lives ranging from about 2 years at Sleeping Bear Dunes to about 5 years at Eagle Harbor.

Table II-10: Atmospheric half-lives and relative standard errors (RSE) of pesticides determined from regression parameters^a

	from regression parameters ^a							
	<i>Eagle Harbor</i>		<i>Sleeping Bear Dunes</i>		<i>Sturgeon Point</i>		<i>Point Petre</i>	
	$t_{1/2}$ (yrs)	RSE	$t_{1/2}$ (yrs)	RSE	$t_{1/2}$ (yrs)	RSE	$t_{1/2}$ (yrs)	RSE
DDT	2.5	25%	2.3	26%	2.7	29%	#	#
DDE	5.1	26%	2.6	21%	7.1	42%	9.2	46%
DDD	2.7	24%	2.6	30%	1.8	20%	8.0	49%
α -HCH	2.9	10%	2.7	16%	4.9	24%	5.0	17%
γ -HCH	3.4	15%	2.2	22%	3.2	23%	7.3	34%
HCB	12.4	40%	3.3	14%	6.8	18%	n/a ^b	n/a ^b
α -Chlordane	*	*	#	#	4.1	34%	6.2	29%
γ -Chlordane	*	*	3.2	42%	3.2	32%	6.5	33%
<i>t</i> -Nonachlor	#	#	3.5	42%	#	#	9.2	48%
Dieldrin	5.2	43%	1.5	17%	2.9	25%	4.8	26%

^a - Half-lives calculated from parameters that are significant at the 95% confidence level.

* - Chlordane related compounds at Eagle Harbor have negative rate constants.

- Data not significant at the 95% confidence level but rates are negative. Burnt Island data have not been shown since the results are not significant at the 95% confidence level.

^b - HCB is not felt to be reliably retained on PUF during the summer season.

It is interesting to note that a simple display of average concentrations as a function of time, such as is shown for PCBs in Figure II-2, does not reveal the temporal trend inherent in the data. The effect of temperature is so strong that it must be included as a regression parameter in order to determine atmospheric changes as a function of time. On the other hand, these trends

can be seen if the data are first normalized to a common reference temperature. Pesticide partial pressures can be adjusted by removing the effect of temperature as follows:

$$P_{288} = P_{meas} \exp \left[\frac{\Delta H_{vap}}{R} \left(\frac{1}{288} - \frac{1}{T_{meas}} \right) \right]$$

Equation II-3: Correction of partial pressure to ambient temperature

where P_{288} is the average partial pressure of each sample at a reference temperature of 288 °K (the average annual temperature of the troposphere), P_{meas} is the partial pressure calculated from the measured concentration, T_{meas} is the average temperature measured at the site during the 24 hour sampling period, and ΔH_{vap} is derived from the a_1 term in equation II.2. Assuming first-order reaction kinetics, the natural logarithm of this adjusted partial pressure can be plotted against time and a rate constant determined from the slope of the line. This is illustrated in Figure II-4 for α -HCH at Sturgeon Point. The half-life calculated from the regression line in Figure II.4 is 4.7 years, which compares well with the half-life of 4.9 years determined from the multiple regression using equation II.2; see Table II-11.

In most cases, the environmental atmospheric half-lives determined for gaseous pesticides at the U.S. sites are well under 4 years, compared to 6 years for PCBs at these same sites. While the introduction of pesticides into the environment has been severely curtailed in the past few decades, PCBs remain in current use in capacitors, transformers, and as ballasts in fluorescent lights. The longer atmospheric half-life of PCBs may be due to their leaking into the atmosphere from these contemporary sources. This illustrates the important distinction between banning the use of a chemical and banning its production.

Finally, the atmosphere is a dynamic system, and it is impossible to account for its normal variations without long-term study. While this study is long compared to other such studies, it is not yet long enough to sufficiently account for normal climatic variability. Thus, it is important to continue to make measurements of these compounds at these sites for several years to come.

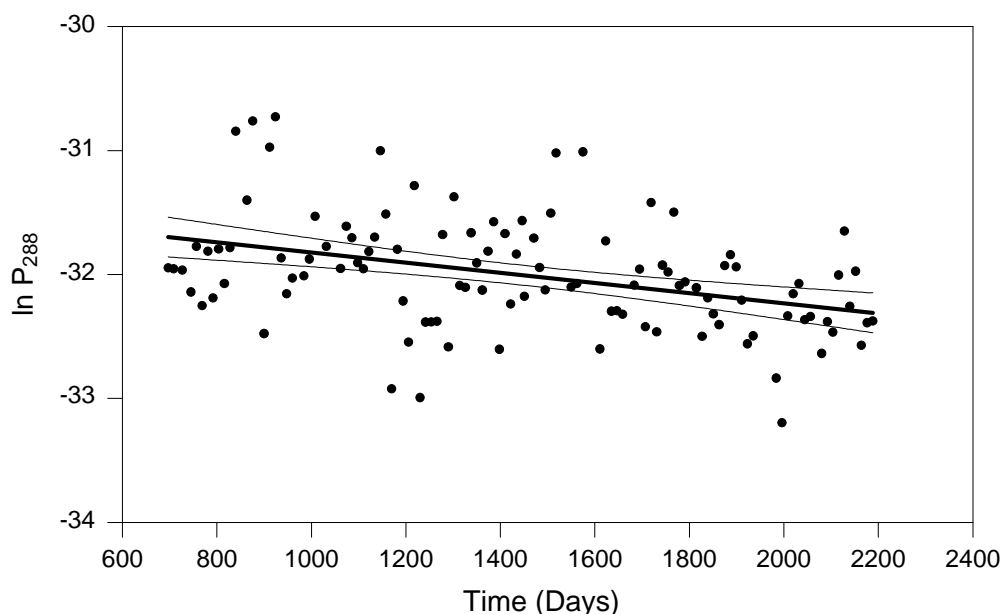


Figure II-4: First order decay of a-HCH at Sturgeon Point. The natural logarithm of the partial pressure, adjusted to a reference temperature of 288 K, is plotted versus the relative Julian day.

II.2.2 Spatial and Temporal Trends in Organic Precipitation Concentrations

As reported by Chan et al. (1994), volume-weighted mean precipitation concentrations of most of the organochlorine pesticides measured in IADN have declined since the late 1980's. This section will present updated trend results for selected chemicals, focusing on results from Sibley (Lake Superior), Pelee Island (Lake Erie) and Point Petre (Lake Ontario) to further illustrate spatial differences.

α -HCH and lindane (γ -HCH) precipitation concentrations were not markedly different among stations (see Figures II-5 and II-6), reflecting their ubiquitous nature. Over the period of record, concentrations of both isomers have declined, although it is interesting to note that between 1991 and 1994, concentrations of lindane have increased steadily at both Sibley and Point Petre from the EHD data. This upward trend for lindane is not seen in the Master Station data from NWRI sampling at Point Petre which shows concentrations of 2.5, 1.5, and 1.7 ng/L

respectively for these three years. Precipitation measurements at Point Petre show a 30-40% variability (Hoff et al., 1996) and thus the differences between the NWRI and EHD results are comparable to this variability.

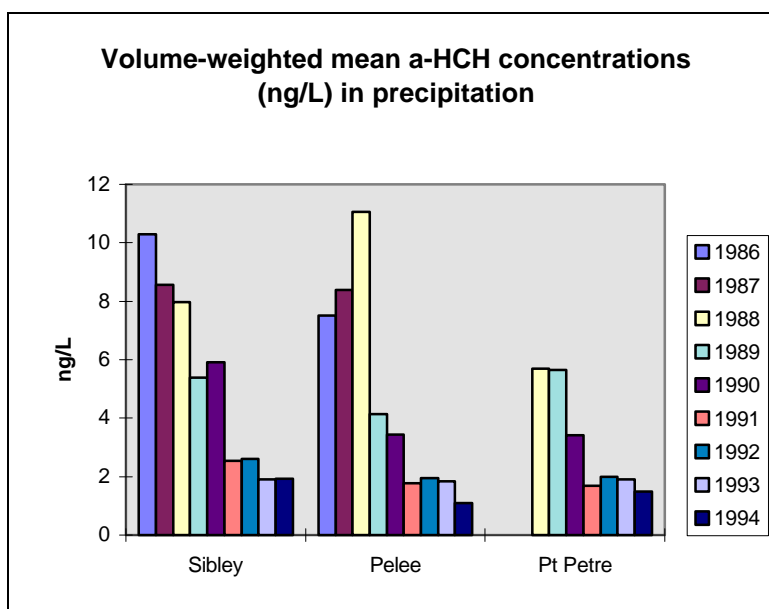


Figure II-5: α -HCH concentration in precipitation from two satellite stations and one master station in Canada (extended from Chan et al., 1994). Concentrations of α -HCH in precipitation are also decreasing with time.

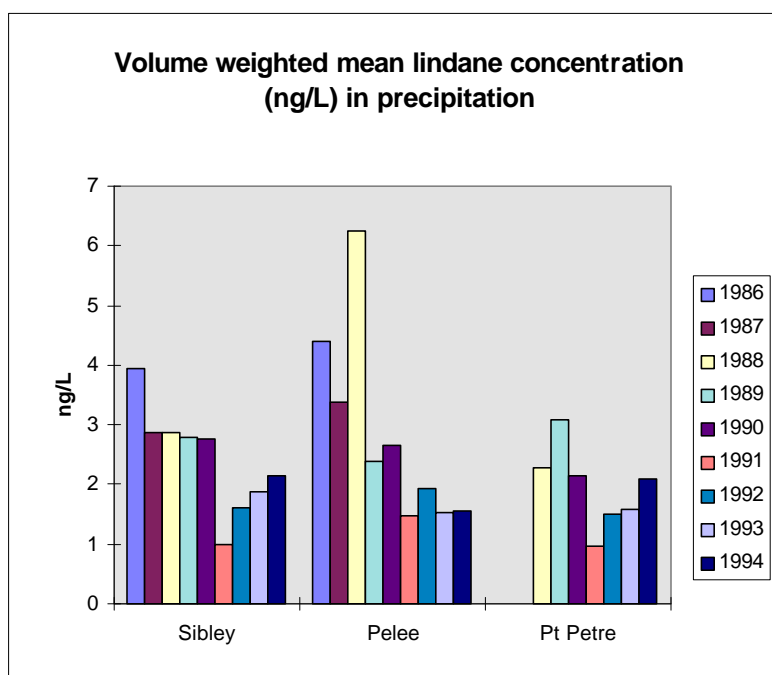


Figure II-6: γ -HCH concentration in precipitation from two satellite stations and one master station in Canada (extended from Chan et al., 1994).

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In Figure II-7, dieldrin concentrations can be seen to have declined between 1986 and 1994. Concentrations at Pelee Island, however, were 3-4 times greater than those observed at the other sites, no doubt because of its proximity to agricultural activities, where usage would be higher.

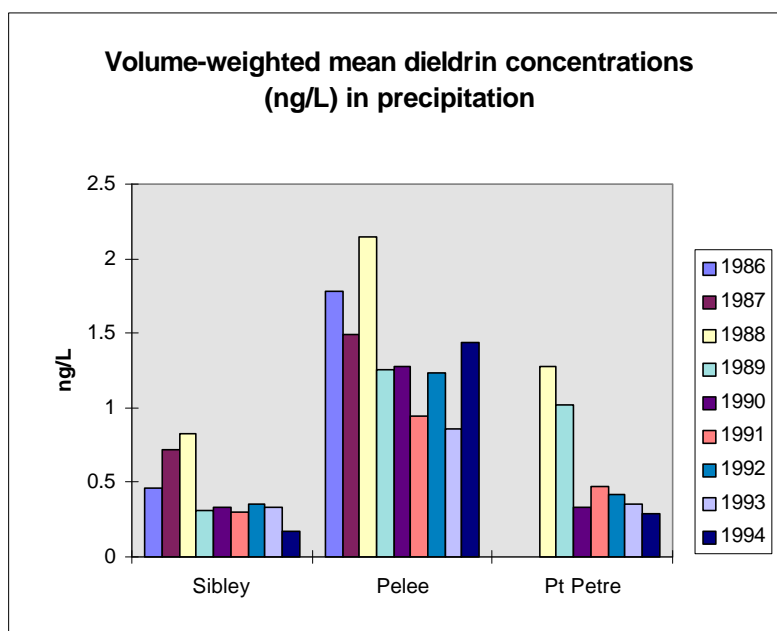


Figure II-7: Dieldrin precipitation concentration time series from the same three EHD sites.

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Trends in precipitation concentrations of β -endosulfan are shown in Figure II-8; similar patterns are observed in the α -isomer, although concentrations are generally half of those observed in the β -isomer. Endosulfan is currently used as a broad-spectrum insecticide for control of wood borers and other insects in greenhouses, nurseries, and on vegetable farms. Due to its continued usage, no decline in concentrations is seen. Seasonally, both isomers exhibit strong concentration peaks in July, consistent with air concentration measurements of endosulfan at Egbert (Hoff et al., 1992a). Pelee Island and Point Petre generally show mean concentrations about twice that of Sibley, with occasional seasonal spikes associated with times of application.

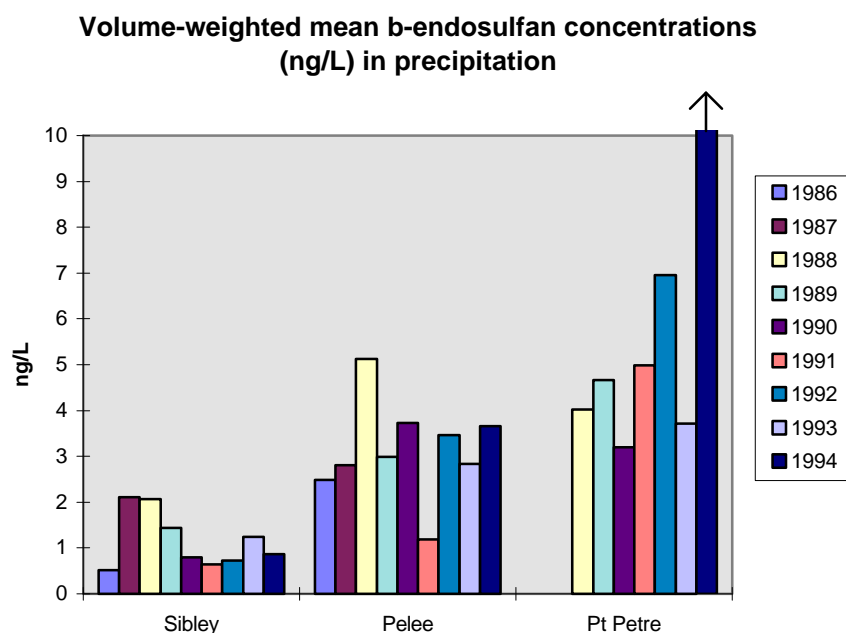


Figure II-8: Endosulphan trends in precipitation for Superior, Erie and Ontario from EHD sites.

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As part of IADN's method development work, precipitation samples throughout the Canadian side of the Great Lakes basin have been analyzed for atrazine and metolachlor, two of the most heavily used pesticides in the Great Lakes basin. In 1993, for example, approximately 14,000 tonnes of atrazine and 12,400 tonnes of metolachlor were used in the US Great Lakes basin states. In Ontario, 600 tonnes of atrazine and 1,300 tonnes of metolachlor were applied. They are applied in May, at the time of seeding or shortly thereafter. The highest precipitation concentrations of atrazine and metolachlor were found at sites along the shore of southern Lake Huron, Lake St. Clair, and Pelee Island. The lowest concentrations were associated with sites from Lake Superior (see Figures II-9 - labeled Figure 4 in graphic and II-10 - labeled Figure 5 in graphic).

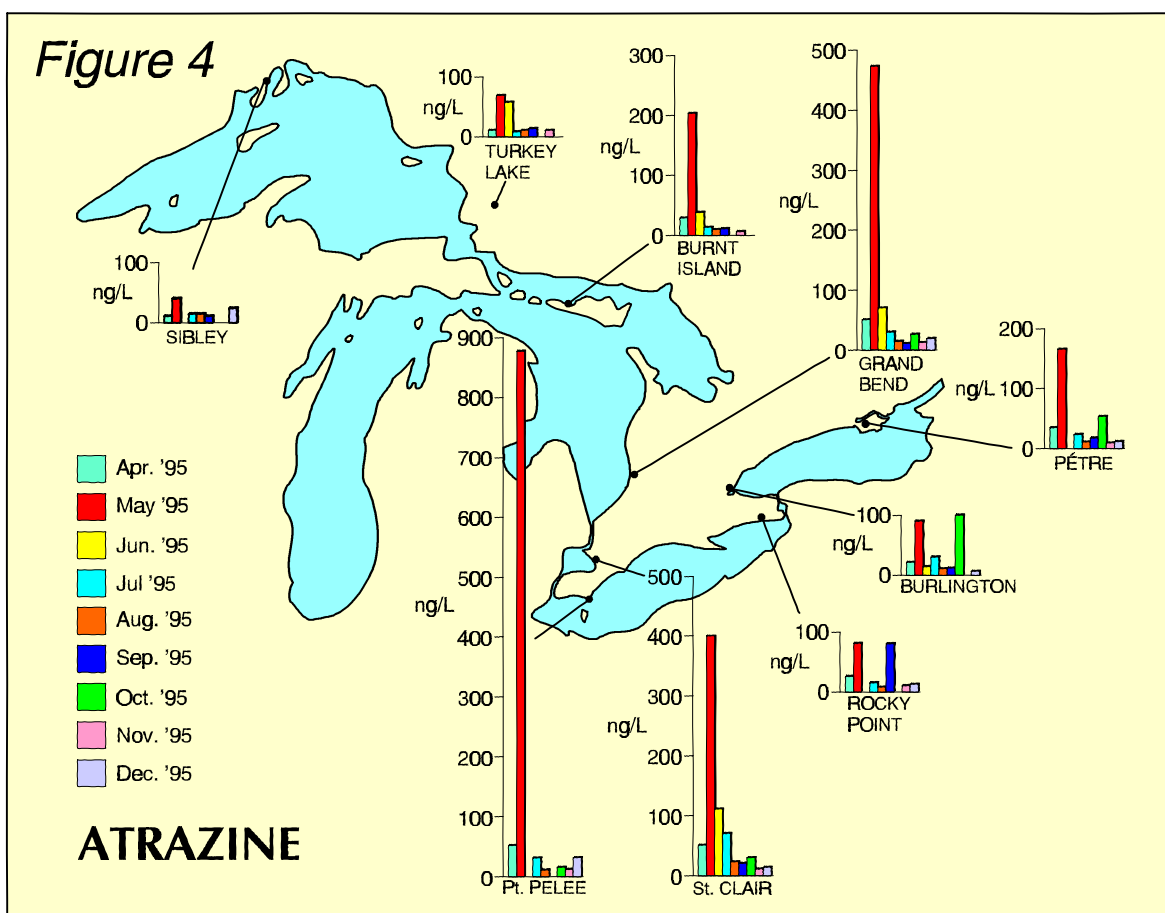


Figure II-9: Concentrations of atrazine in precipitation measured at the EHD sites. The time axes runs from April to December 1995 and shows the annual usage cycle.

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Maximum concentrations of metolachlor and atrazine were measured during the month of May, at 1120 and 875 ng/L, respectively, about twenty times higher than other months. The spatial and temporal distribution of these herbicides in precipitation correspond to their application time and usage patterns in the basin.

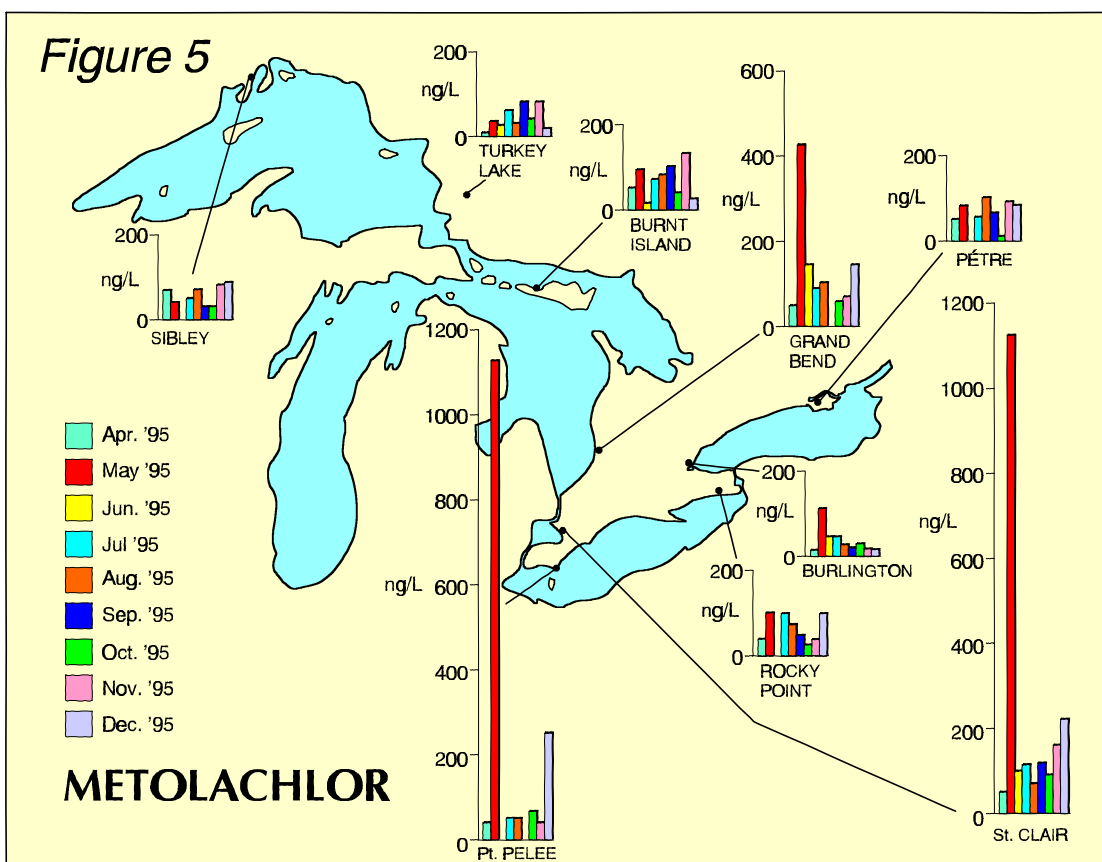


Figure II-10: Concentrations of metolachlor in precipitation measured at the EHD sites. The time axes runs from April to December 1995 and shows the annual usage cycle.

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II.3 Loading Results from the IADN data

The mandate given by Annex 15 and the IADN IP1 was to determine loadings to the Great Lakes on a biennial basis. The first IJC Workshop report (Strachan and Eisenreich, 1988) had tremendous impact in raising the awareness of atmospheric deposition as a major factor in controlling lakewide concentrations of toxic chemicals. In 1992, a follow-up workshop, led by the Grey Freshwater Institute of the University of Minnesota, revised the 1988 estimates based on more current data. Much of the revised data that went into this work was from measurements being made at what are now IADN sites, the 1988/9 Egbert study (Hoff et al., 1992a, 1992b), Environment Canada precipitation-only sites (Chan et al., 1994), and preliminary unpublished IADN data. In 1992, the second group of estimates of wet and dry deposition of toxic chemicals were published (Eisenreich and Strachan, 1992).

In 1994, a workshop was held at Windsor, Ontario, to use the IADN data, along with supplementary information from research efforts on the Great Lakes, to make estimates (Hoff et al., 1996) of the loadings of toxics chemicals to each of the lakes with data focusing on the 1992 sampling year (data from 1991-1993 were also consulted). This work expanded the efforts of the 1988 IJC study by including a wider range of chemicals (14 in all) which were examined not only for their dry and wet deposition loadings to the lakes, but also for their gas transfer component. The conclusion drawn in the study was that gas transfer is the most important, if not dominant, component of the loading for most of the organochlorine compounds studied.

The procedure for calculating loadings for the IADN program were detailed in Hoff et al., 1996. The loading equations included here are:

$$\begin{aligned}
 L = & F_t \mathbf{f}_t C_t && [atmospheric - tributary] \\
 & + C_p R_p A_p && [wet deposition] \\
 & + A K_{oL} (1 - \mathbf{f}_a) C_a \frac{RT}{H} && [gas absorption] \\
 & + \mathbf{f}_a A C_a v_d && [dry deposition] \\
 V = & A K_{oL} (1 - \mathbf{f}_w) C_w && [volatilization]
 \end{aligned}$$

Equation II-4: Loading equations

Wet deposition is calculated from the rain rate, R_p , the area of the precipitation, A_p , and the concentration in precipitation, C_p . Since these variables are directly measured in the IADN program, wet deposition is the only unambiguous term in the loading equation. The atmospheric component of the tributary flux (from the tributary flow, F_t , the fraction of the tributary loading which is atmospheric in origin, f_t , and the concentration in the tributary, C_t) has not been measured to date and was estimated in Dolan et al. (1993) to be about 10% of the total wet load. This has never been confirmed by measurement. The dry deposition term is calculated by measuring the particulate concentration in air, $f_a C_a$, and multiplying by an assumed deposition velocity (v_d). This deposition velocity is the same for all particles and is estimated to be 0.2 cm s^{-1} (Strachan and Eisenreich, 1988). Clearly, if the SVOCs or metals are on coarse particles, this deposition velocity will be too small. A represents the area of the lakes.

The gas exchange terms (volatilization and gas absorption) are more difficult to solve. Henry's law constants (H) must be known from the literature or assumed to be similar to other compounds in the same class. Mass transfer velocities, K_{ol} , are calculated from the mean wind speed using the methods of Mackay and Yuen (1983) and Schwarzenbach et al. (1993). Water concentrations, C_w , are not routinely measured at the same frequency as the IADN data and, therefore, must be taken from the literature.

In all these terms, a mean lakewide seasonal average concentration is determined using the results from all stations which are available on each lake. There is some degree of subjectivity in the calculation when there are widely disparate measures of the concentration from different sites or agencies. In general, however, a simple seasonal and annual averaging of the data from the different sites was used. If there were large spatial gradients in concentration (due to urban areas, for example), the IADN loadings could be underestimates of the total loading to the lakes.

Table II-12 gives a summary of the concentration data, which were used in the Hoff et al. (1996) and Hillery et al. (1997c) papers, for 1992 and 1993/94, respectively.

Table II-11: Concentration Data from IADN Master Stations Annual Averages

Species	Year	Superior			Michigan			Huron			Erie			Ontario		
		Precip Conc(ng/L)	Particle pg/m3	Gas pg/m3	Precip Conc(ng/L)	Particle pg/m3	Gas pg/m3	Precip Conc(ng/L)	Particle pg/m3	Gas pg/m3	Precip Conc(ng/L)	Particle pg/m3	Gas pg/m3	Precip Conc(ng/L)	Particle pg/m3	Gas pg/m3
A-HCH	1992	1.40	0.22	112.00	1.40	0.33	123.00	3.30	#N/A	#N/A	1.50	0.50	163.00	2.80	0.00	79.00
	1993	0.63	1.26	112.40	0.63	1.11	126.40	2.61	#N/A	42.48	1.06	1.38	165.00	1.72	#N/A	44.15
	1994	1.40	0.22	124.00	1.40	0.33	126.70	3.72	#N/A	41.25	1.50	0.50	163.70	2.19	#N/A	52.32
G-HCH	1992	1.20	0.12	32.00	1.60	0.26	210.00	2.30	#N/A	#N/A	1.30	0.20	56.00	2.50	0.10	27.00
	1993	0.20	0.55	17.70	1.65	0.53	52.80	4.64	#N/A	10.35	0.78	0.80	51.40	1.46	#N/A	15.15
	1994	1.20	0.12	14.90	1.60	0.26	49.60	3.07	#N/A	12.57	1.30	0.20	43.90	1.65	#N/A	18.75
Dieldrin	1992	0.40	1.50	14.00	0.99	1.90	34.00	0.18	#N/A	#N/A	0.80	3.20	30.00	0.60	1.60	23.00
	1993	0.60	1.31	11.20	0.65	2.25	39.50	0.25	#N/A	13.00	0.96	2.55	52.40	0.24	#N/A	23.52
	1994	0.40	1.50	13.50	0.99	1.90	36.30	0.35	#N/A	12.33	0.80	3.20	36.40	0.20	#N/A	21.85
p,p' - DDE	1992	0.06	0.08	2.50	0.09	0.13	11.00	0.14	#N/A	#N/A	0.20	0.30	18.00	0.20	0.10	16.00
	1993	0.09	0.24	2.80	0.10	0.40	13.50	0.03	#N/A	2.70	0.13	0.42	28.10	0.07	#N/A	14.99
	1994	0.06	0.08	1.90	0.09	0.13	9.10	0.09	#N/A	2.59	0.20	0.30	25.80	0.05	#N/A	20.25
p,p'-DDT	1992	0.20	0.30	3.90	0.47	0.45	9.40	0.31	#N/A	#N/A	1.40	2.20	13.00	0.20	3.60	7.00
	1993	0.93	0.39	2.40	0.93	1.97	7.80	0.01	#N/A	0.80	2.73	1.23	16.20	0.21	#N/A	3.93
	1994	0.20	0.30	2.60	0.47	0.45	4.40	0.11	#N/A	0.86	1.40	2.20	10.20	0.08	#N/A	5.19
p,p' -DDD	1992	#N/A	1.20	1.50	#N/A	1.10	3.70	0.10	#N/A	#N/A	0.09	1.30	7.70	0.20	1.00	2.30
	1993	0.22	0.02	0.60	0.12	0.32	2.20	0.03	#N/A	0.18	0.09	0.16	4.50	0.01	#N/A	0.50
	1994	#N/A	1.20	1.00	#N/A	1.10	1.50	0.05	#N/A	0.09	0.09	1.30	2.60	0.04	#N/A	0.65
HCB	1992	0.10	0.20	98.00	0.06	0.10	120.00	0.13	#N/A	0.05	0.04	0.20	80.00	0.30	0.10	130.00
	1993	0.37	3.91	68.00	0.25	3.56	87.40	0.18	#N/A	31.12	0.15	4.18	101.70	0.11	#N/A	33.75
	1994	0.10	0.20	70.20	0.06	0.10	77.50	0.08	#N/A	28.22	0.04	0.20	83.50	0.04	#N/A	43.29
PCB18	1992	0.02	0.05	4.80	0.02	0.05	7.80	0.21	#N/A	#N/A	0.02	0.09	20.00	0.20	0.06	9.80
	1993	0.04	0.08	3.90	0.02	0.11	7.20	0.07	#N/A	5.42	0.01	0.15	15.30	0.02	#N/A	8.80
	1994	0.02	0.05	4.20	0.02	0.05	6.20	0.03	#N/A	4.70	0.02	0.09	11.20	0.02	#N/A	10.25
PCB44	1992	0.03	0.10	3.40	0.03	0.09	9.70	0.32	#N/A	#N/A	0.02	0.20	14.00	0.20	0.10	6.60
	1993	0.14	0.21	4.80	0.02	0.19	10.40	0.10	#N/A	1.29	0.02	0.28	16.20	0.24	#N/A	3.53
	1994	0.03	0.10	7.70	0.03	0.09	4.20	0.05	#N/A	1.23	0.02	0.20	12.40	0.04	#N/A	4.10
PCB52	1992	0.02	0.06	4.20	0.02	0.06	6.40	0.12	#N/A	#N/A	0.02	0.20	16.00	0.08	0.06	6.80
	1993	0.02	0.11	5.10	0.03	0.14	7.20	0.19	#N/A	1.87	0.02	0.21	16.70	0.06	#N/A	5.01
	1994	0.02	0.06	9.90	0.02	0.06	5.90	0.07	#N/A	2.19	0.03	0.20	15.30	0.06	#N/A	6.64
PCB101	1992	0.04	0.10	2.30	0.03	0.09	4.00	0.14	#N/A	#N/A	0.02	0.20	9.80	0.10	0.09	3.30
	1993	0.02	0.15	3.80	0.01	0.17	5.00	0.10	#N/A	1.16	0.02	0.23	10.50	0.09	#N/A	3.53
	1994	0.04	0.10	8.40	0.03	0.09	3.40	0.05	#N/A	1.45	0.03	0.20	8.40	0.04	#N/A	5.29
Sum-PCB	1992	1.20	5.60	90.00	1.05	4.90	160.00	2.50	#N/A	#N/A	0.70	8.80	360.00	3.10	4.70	170.00
	1993	1.83	5.03	127.60	2.42	6.04	183.00	2.32	#N/A	45.33	0.73	8.86	355.80	3.94	#N/A	83.74
	1994	1.35	17.61	192.40	1.34	11.59	136.20	2.28	#N/A	56.93	1.12	17.55	253.80	0.98	#N/A	145.84

Table II-12 Concentration Data from IADN Master Stations Annual Averages (continued)

PHEN	1992	3.70	19.00	860.00	5.50	26.00	920.00	#N/A	#N/A	#N/A	11.00	60.00	4000.00	3.20	37.00	760.00
	1993	1.90	12.04	572.50	2.05	22.95	1196.00	11.51	23.67	#N/A	11.09	62.84	5274.00	34.55	23.83	#N/A
	1994	3.70	19.00	860.00	5.50	26.00	920.00	8.21	16.75	#N/A	11.00	60.00	4000.00	18.09	34.88	#N/A
PYR	1992	2.70	22.00	190.00	4.00	35.00	97.00	#N/A	#N/A	#N/A	8.20	74.00	510.00	3.40	58.00	190.00
	1993	1.47	14.82	49.10	2.14	34.93	120.00	7.20	34.01	#N/A	9.13	81.42	500.00	20.09	48.40	#N/A
	1994	2.70	22.00	190.00	4.00	35.00	97.00	4.44	20.00	#N/A	8.20	74.00	510.00	16.70	38.79	#N/A
B(k)F	1992	2.70	22.00	19.00	2.60	13.00	17.10	#N/A	#N/A	#N/A	8.20	74.00	19.00	3.40	58.00	2.60
	1993	1.23	3.10	2.40	1.16	10.69	2.50	#N/A	22.30	#N/A	3.60	54.45	2.50	#N/A	55.73	#N/A
	1994	2.70	22.00	19.00	2.60	13.00	17.10	#N/A	11.78	#N/A	8.20	74.00	19.00	#N/A	26.64	#N/A
B(a)P	1992	2.90	11.00	9.30	3.80	21.00	10.40	#N/A	#N/A	#N/A	5.10	44.00	13.00	3.00	45.00	3.00
	1993	1.45	2.38	8.90	1.81	8.88	9.10	#N/A	28.06	#N/A	5.04	35.92	9.20	#N/A	54.19	#N/A
	1994	2.90	11.00	9.30	3.80	21.00	10.40	#N/A	14.27	#N/A	5.10	44.00	13.00	#N/A	36.00	#N/A
Pb	1992	700.00	2500.00	#N/A	1100.00	4800.00	#N/A	1400.00	4800.00		1700.00	11000.00	#N/A	2400.00	3700.00	#N/A
	1993	#N/A	3200.00	#N/A	#N/A	3600.00	#N/A	1170.00	2252.00	#N/A	#N/A	8300.00	#N/A	1420.00	4537.00	#N/A
	1994	#N/A	3980.00	#N/A	#N/A	3900.00	#N/A	890.00	2760.00	#N/A	#N/A	8110.00	#N/A	970.00	5340.00	#N/A
As	1992	200.00	700.00	#N/A	100.00	500.00	#N/A	100.00	410.00		200.00	1100.00	#N/A	200.00	480.00	#N/A
	1993	#N/A	1000.00	#N/A	#N/A	200.00	#N/A	140.00	417.00	#N/A	#N/A	1000.00	#N/A	170.00	646.00	#N/A
	1994	#N/A	430.00	#N/A	#N/A	470.00	#N/A	120.00	322.00	#N/A	#N/A	900.00	#N/A	140.00	498.00	#N/A
Se	1992	600.00	300.00	#N/A	400.00	800.00	#N/A	200.00	530.00		700.00	1500.00	#N/A	300.00	830.00	#N/A
	1993	#N/A	350.00	#N/A	#N/A	250.00	#N/A	210.00	640.00	#N/A	#N/A	1900.00	#N/A	270.00	1436.00	#N/A
	1994	#N/A	470.00	#N/A	#N/A	800.00	#N/A	190.00	728.00	#N/A	#N/A	1600.00	#N/A	260.00	1410.00	#N/A
Cd	1992	250.00	500.00	#N/A	200.00	300.00	#N/A	100.00	90.00		130.00	800.00	#N/A	200.00	70.00	#N/A
	1993	#N/A	400.00	#N/A	#N/A	1500.00	#N/A	50.00	93.00	#N/A	#N/A	600.00	#N/A	70.00	101.00	#N/A
	1994	#N/A	560.00	#N/A	#N/A	580.00	#N/A	40.00	102.00	#N/A	#N/A	350.00	#N/A	40.00	124.00	#N/A

#N/A - not available - not measured

Figure II-11 is a diagram from Hoff et al. (1996) showing that, as a percentage of the total loading of chemical to Lake Ontario, for example, gas absorption is a significant proportion of the total. The diagram also shows that wet and dry deposition become dominant for non-gaseous compounds such as the metals, Pb, Cd, As, and Se, and for the heavier PAHs, such as B(k)F and B(a)P. The work also showed that some chemicals are in equilibrium with the lake concentrations (α -HCH, for example has volatilization equal to the inputs on an annual basis). Given the uncertainty in the estimates and the fact that water concentrations were taken from the literature and poorly known, it is not improbable that all the gas-phase compounds are in near equilibrium with the lake. A recent paper (Mackay and Bentzen, 1997) has used these results to emphasize that control of the concentrations of the chemical in the air column is more important than addressing water-side sources of many of these compounds.

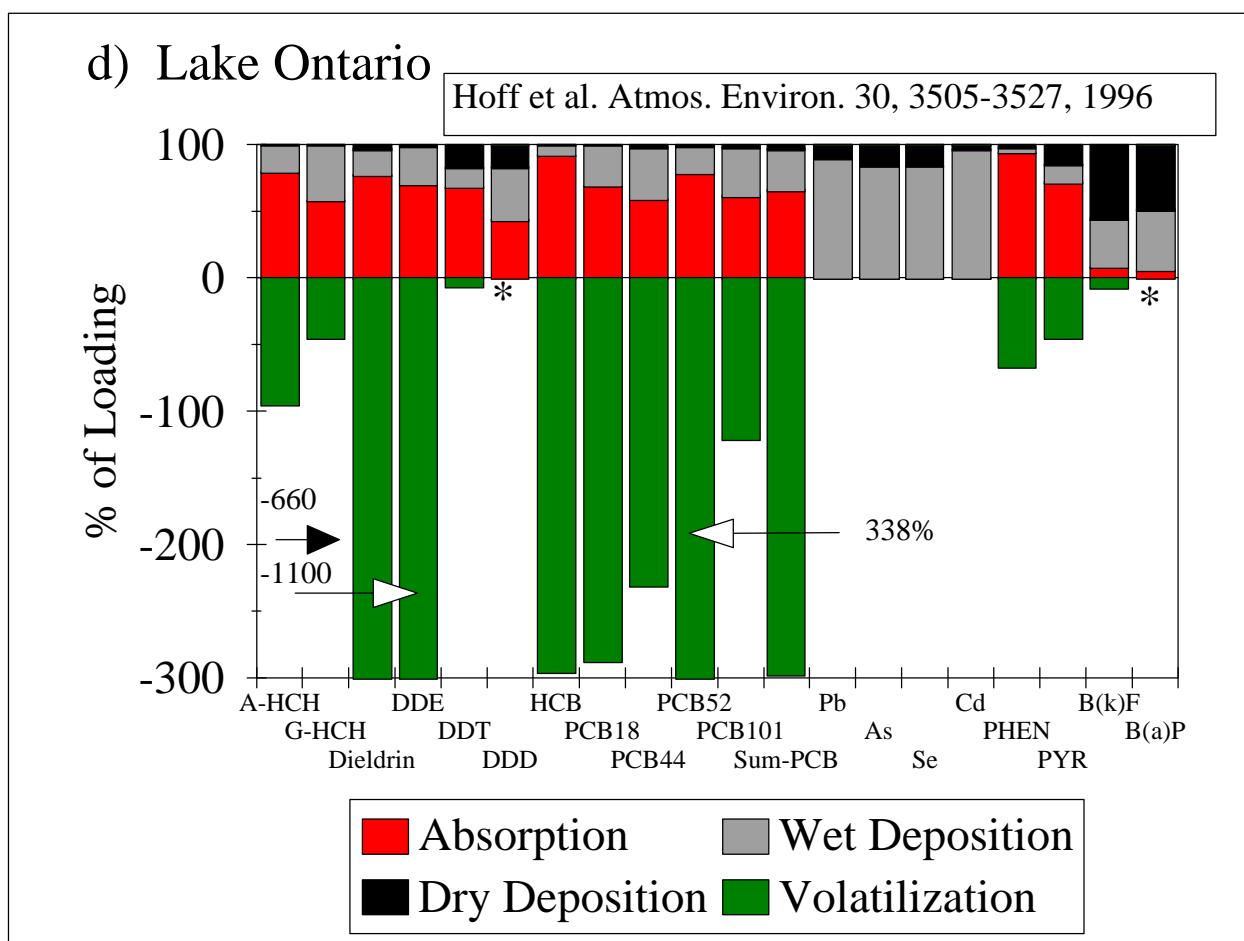


Figure II-11: Percentage of the deposition to the lake which is due to gas phase absorption, wet deposition and dry deposition (totaling 100%) and the opposing flux of volatilization from the lakes as a proportion of that total (from Hoff et al., 1996). * indicates that there is no available water concentration data.

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A recent book chapter by IADN participants (Hillery et al, 1997b) reviewed the comparison between the early 1980, late 1980 and early 1990 estimates. A new set of estimates of the loadings to the Great Lakes in kg y^{-1} has been prepared (Hillery et al., 1997c). These estimates repeat the exercise of the 1994 workshop and include the wet and dry deposition and gas transfer for the same 14 chemicals as in the Hoff et al. (1996). Table II-13 shows the comparison of the loadings from those studies.

Table II-12: Intercomparison of Loading Estimates for the Great Lakes (kg y^{-1})

Chemical	Superior	Michigan	Huron	Erie	Ontario
Σ - PCBs (Wet+Dry)					
1980-86	550	400	400	180	140
1980-90	160	110	110	53	42
1991-92	85	69	180 ^b	37	64
1993-94	160	140	140 ^b	60	60 ^b
Σ - PCBs (Net Gas)					
1980-86	-1900	-5140	-2560	-1100	-708
1991-92	-1700	-2700	na	-420	-440
1993-94	-1430	-2700	-670	-450	-470
Σ-DDT (Wet + Dry)					
1980-86	90	64	65	33	26
1980-90	34	25	25	12	10
1991-92	17	32	37 ^b	46	16
1993-94	80	60	9 ^b	80	10 ^b
Σ - DDT(Net Gas)					
1980-86	-681	-480	-495	-213	-162
1991-92	30	67	na	34	13
1993-94	15	36	4	36	8
B(a)P (Wet and Dry)					
1980-86	69	180	180	81	62
1980-90	120	84	84	39	31
1991-92	200	250	na	240	120
1993-94	160	180	80 ^c	260	60 ^c
Pb (Wet + Dry)					
1980-86	230,000	540,000	400,000	230,000	220,000
1980-90	67,000	26,000	10,000	97,000	48,000
1991-92	51,000	72,000	100,000 ^b	65,000	45,000
1993-94	46,000 ^d	41,000 ^d	77,000	33,000 ^d	31,000

^a Data for 1980-86 is from Strachan and Eisenreich (1988), 1980-90 is from Eisenreich and Strachan (1992), 1991-92 is from Hoff et al. (1996), and 1993-94 is from Hillery et al. (1997).

^b Wet Deposition Only

^c Dry deposition only

^d Partial year data for wet deposition

It is difficult to make lake-to-lake comparison on the total loadings to each lake because of the difference in their sizes. Table II-14 shows the net fluxes from the 1991-2 and 1993-94 data in $\text{ng m}^2 \text{d}^{-1}$ for the SVOC species and Table II-15 shows the flux for the metals in $\mu\text{g m}^2 \text{d}^{-1}$.

Table II-13: Fluxes of Semivolatile Organic Compounds to the Great Lakes

Species	Year	Superior			Michigan			Huron			Erie			Ontario		
		Wet ng m ² d ⁻¹	Dry ng m ² d ⁻¹	Net Gas ng m ² d ⁻¹	Wet ng m ² d ⁻¹	Dry ng m ² d ⁻¹	Net Gas ng m ² d ⁻¹	Wet ng m ² d ⁻¹	Dry ng m ² d ⁻¹	Net Gas ng m ² d ⁻¹	Wet ng m ² d ⁻¹	Dry ng m ² d ⁻¹	Net Gas ng m ² d ⁻¹	Wet ng m ² d ⁻¹	Dry ng m ² d ⁻¹	Net Gas ng m ² d ⁻¹
α -HCH	1991-92	2.60	0.04	12.00	3.00	0.07	-6.80	7.60	-	-	9.00	0.13	11.00	7.50	0.00	-5.80
	1993	1.50	0.19	14.00	2.00	0.19	-5.10	7.60	-	-36.00	3.70	0.21	40.00	5.00	-	-11.00
	1994	2.00	0.11	17.00	3.10	0.05	-4.30	8.40	-	-36.00	6.00	0.14	43.00	6.20	-	-8.70
γ -HCH	1991-92	2.10	0.02	4.60	3.10	0.05	59.00	6.40	-	-	4.90	0.05	6.50	7.20	0.03	2.30
	1993	0.46	0.09	0.72	6.40	0.09	16.00	16.00	-	-3.40	2.70	0.14	11.00	5.90	-	-1.30
	1994	2.00	0.05	0.17	3.10	0.05	10.00	7.00	-	-2.30	4.50	0.07	11.00	4.50	-	-0.11
Dieldrin	1991-92	0.71	0.25	-26.00	2.70	0.38	-	0.50	-	-	3.00	0.60	-65.00	1.50	0.24	-46.00
	1993	2.70	0.21	-27.00	2.00	0.34	-	0.81	-	-48.00	3.60	0.40	-21.00	0.87	-	-26.00
	1994	0.24	0.30	-26.00	2.60	0.46	-	0.87	-	-48.00	2.80	0.62	-24.00	0.56	-	-26.00
DDE	1991-92	0.09	0.01	-	0.18	0.02	-	0.50	-	-	0.49	0.06	-	0.64	0.03	-24.00
	1993	0.14	0.04	-	0.35	0.07	-	0.09	-	NA	0.55	0.07	-	0.32	-	-24.00
	1994	0.16	0.03	-	0.17	0.03	-	0.21	-	-	0.47	0.08	-	0.11	-	-24.00
DDT	1991-92	0.21	0.05	1.00	1.10	0.11	3.20	1.00	-	-	3.60	0.46	3.70	0.47	0.53	1.90
	1993	3.40	0.06	0.58	2.70	0.30	2.50	0.03	-	0.17	11.00	0.22	5.10	1.10	-	0.88
	1994	0.50	0.06	0.42	2.00	0.06	0.96	0.25	-	0.19	4.20	0.27	2.80	0.19	-	1.40
DDD	1991-92	-	0.20	-	-	0.18	-	-	-	-	0.20	0.21	-	0.42	0.18	-
	1993	0.71	0.00	-	0.38	0.05	-	0.10	-	-	0.38	0.02	-	0.06	-	-
	1994	-	0.18	-	-	0.15	-	0.11	-	-	0.24	0.17	-	0.09	-	-
HCB	1991-92	0.18	0.02	3.50	0.13	0.02	2.00	0.27	-	-	0.09	0.02	-4.80	0.89	0.02	-22.00
	1993	1.10	0.63	0.91	0.77	0.61	-0.74	0.54	-	-1.70	0.63	0.69	-1.80	0.47	-	-28.00
	1994	0.36	0.23	0.65	0.18	0.13	-2.20	0.19	-	-2.00	0.16	0.23	-3.80	0.11	-	-28.00
PCB18	1991-92	0.03	0.01	-4.30	0.04	0.01	-7.20	0.78	-	-	0.04	0.01	-	0.37	0.01	-2.70
	1993	0.12	0.01	-4.30	0.07	0.02	-7.30	0.21	-	-1.90	0.07	0.02	-4.10	0.04	-	-2.70
	1994	0.05	0.06	-4.40	0.10	0.04	-7.50	0.06	-	-1.90	0.05	0.05	-4.40	0.06	-	-2.70
PCB44	1991-92	0.05	0.02	-1.10	0.07	0.02	-4.50	0.93	-	-	0.06	0.03	-1.30	0.52	0.03	-2.30
	1993	0.30	0.03	-0.82	0.06	0.03	-4.10	0.30	-	-0.67	0.09	0.05	-0.86	0.92	-	-2.60
	1994	0.06	0.06	-0.62	0.08	0.04	-5.10	0.14	-	-0.67	0.06	0.06	-1.40	0.12	-	-2.60
PCB52	1991-92	0.04	0.01	-0.83	0.06	0.01	-6.00	0.35	-	-	0.05	0.03	-1.70	0.23	0.01	-2.80
	1993	0.08	0.02	-0.58	0.08	0.03	-5.70	0.58	-	-0.51	0.08	0.04	-1.40	0.21	-	-3.10
	1994	0.07	0.06	-0.04	0.10	0.02	-6.20	0.15	-	-0.48	0.08	0.05	-1.80	0.16	-	-2.90
PCB101	1991-92	0.06	0.02	-2.90	0.07	0.02	-3.10	0.50	-	-	0.05	0.03	-0.70	0.25	0.01	-0.41
	1993	0.06	0.03	-2.60	0.05	0.03	-2.80	0.31	-	0.03	0.09	0.04	-0.50	0.37	-	-0.40
	1994	0.06	0.04	-2.10	0.09	0.03	-3.20	0.11	-	0.06	0.07	0.05	-0.92	0.11	-	-0.24

Species	Year	Superior			Michigan			Huron			Erie			Ontario		
		Wet ng m ² d ⁻¹	Dry ng m ² d ⁻¹	Net Gas ng m ² d ⁻¹	Wet ng m ² d ⁻¹	Dry ng m ² d ⁻¹	Net Gas ng m ² d ⁻¹	Wet ng m ² d ⁻¹	Dry ng m ² d ⁻¹	Net Gas ng m ² d ⁻¹	Wet ng m ² d ⁻¹	Dry ng m ² d ⁻¹	Net Gas ng m ² d ⁻¹	Wet ng m ² d ⁻¹	Dry ng m ² d ⁻¹	Net Gas ng m ² d ⁻¹
Σ-PCB	1991-92	1.90	0.89	-56.00	2.50	0.78	-130.00	8.30			2.30	1.70	-45.00	8.20	0.80	-61.00
	1993	4.90	0.82	-50.00	6.60	1.10	-120.00	7.00	-	-32.00	3.00	1.50	-40.00	15.00	-	-70.00
	1994	2.10	2.90	-45.00	3.30	1.90	-130.00	6.10	-	-32.00	4.40	3.10	-55.00	2.70	-	-64.00
PHEN	1991-92	8.50	3.30	-110.00	17.00	5.20	-	-			53.00	9.10	-	10.00	6.70	69.00
	1993	6.40	2.00	-180.00	9.10	4.80	-	34.00	4.20	-	40.00	11.00	-	81.00	3.70	69.00
	1994	4.60	4.00	-130.00	10.00	4.30	-	18.00	3.20	-	41.00	14.00	-	73.00	6.40	69.00
PYR	1991-92	5.30	3.90	53.00	10.00	6.80	-	-			35.00	12.00	-	9.30	10.00	18.00
	1993	5.20	2.50	6.10	8.50	6.80	-	19.00	5.90	-	35.00	14.00	-	71.00	7.90	-
	1994	4.80	4.40	47.00	8.90	5.60	-	11.00	3.50	-	32.00	18.00	-	44.00	6.90	-
B(k)F	1991-92	4.00	1.70	6.50	6.10	2.60	-	-			16.00	6.40	-	4.80	7.20	-0.03
	1993	4.70	0.45	0.95	4.30	2.00	-	-	3.80	-	16.00	9.00	-	-	11.00	-
	1994	4.80	4.40	47.00	8.90	5.60	-	11.00	3.50	-	32.00	18.00	-	44.00	6.90	-
B(a)P	1991-92	4.60	1.90	2.90	7.90	3.70	-	-			19.00	6.70	-	7.90	8.40	-
	1993	5.50	0.47	2.80	6.40	2.00	-	-	4.90	-	22.00	6.10	-	-	11.00	-
	1994	3.20	1.50	2.00	5.80	2.80	-	-	2.60	-	18.00	9.10	-	-	6.20	-

Table II-14: Fluxes of Trace Elements to the Great Lakes

Species	Year	Superior		Michigan		Huron		Erie		Ontario	
		Wet µg m ² d ⁻¹	Dry µg m ² d ⁻¹	Wet µg m ² d ⁻¹	Dry µg m ² d ⁻¹	Wet µg m ² d ⁻¹	Dry µg m ² d ⁻¹	Wet µg m ² d ⁻¹	Dry µg m ² d ⁻¹	Wet µg m ² d ⁻¹	Dry µg m ² d ⁻¹
Pb	1991-92	1.30	0.43	2.60	0.83	4.60	0.53	5.00	1.90	5.80	0.64
	1993	NA	0.52	NA	0.80	3.50	0.37	NA	1.40	4.10	0.76
	1994	NA	0.90	NA	NA	2.70	0.50	NA	1.40	2.90	0.89
As	1991-92	0.36	0.12	0.24	0.09	0.49	0.10	0.59	0.19	0.42	0.08
	1993	NA	0.19	NA	0.04	0.30	0.08	NA	0.16	0.48	0.10
	1994	NA	0.10	NA	0.06	0.36	0.05	NA	0.15	0.40	0.09
Se	1991-92	1.10	0.05	0.95	0.14	0.77	0.10	2.10	0.26	0.80	0.15
	1993	NA	0.06	NA	0.04	0.63	0.11	NA	0.30	0.78	0.23
	1994	NA	0.10	NA	NA	0.58	0.12	NA	0.26	0.74	0.26
Cd	1991-92	0.46	0.09	0.47	0.05	0.30	0.02	0.38	0.14	0.37	0.01
	1993	NA	0.07	NA	0.21	0.14	0.01	NA	0.11	0.21	0.01
	1994	NA	0.15	NA	NA	0.13	0.02	NA	0.16	0.10	0.02

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Examination of data in Tables II-14 and II-15 shows that for many compounds there are some systematic differences in the loading of chemical from lake to lake. Figure II-12 shows the wet and dry deposition, gas absorption and gas volatilization of DDT species and HCB by lake for the 1994 year. Gas phase absorption is the most important loading factor for the DDT species, however, HCB appears to be volatilizing out of the lakes. DDT shows large inputs via wet deposition for 1994 for Lakes Erie and Michigan and this deserves further study. There may be more information from the satellite stations that can specify whether this is only occurring at the Master Stations or is an artifact. Dry deposition is relatively unimportant for these gas phase species.

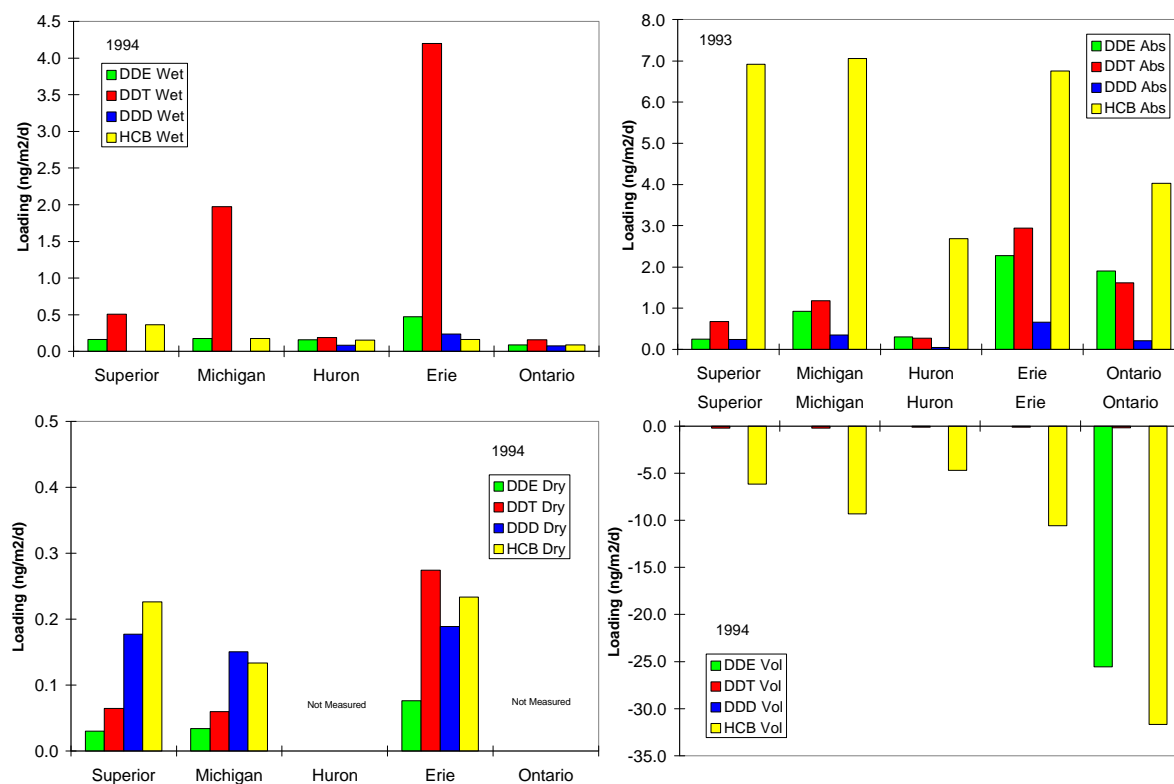


Figure II-12: Wet deposition, dry deposition, gas absorption and gas volatilization for the DDT species for the 1993 year by lake. The volatilization is driven by differences in the water column concentrations which are identical to those given in Hoff et al. (1996)

Figure II-13 shows a similar diagram for the PCB congeners. There appears to be little systematic pattern of deposition from lake to lake and uniformity of deposition is a feature for PCBs. Volatilization exceeded deposition and thus the lakes are outgassing to the atmosphere.

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The Canadian sites no longer estimate PCB dry deposition but it appears from the US data that dry and wet deposition are nearly equal in importance. This was not the case from the 1992 PCB data from Canada (Hoff et al., 1996) and this requires further scrutiny.

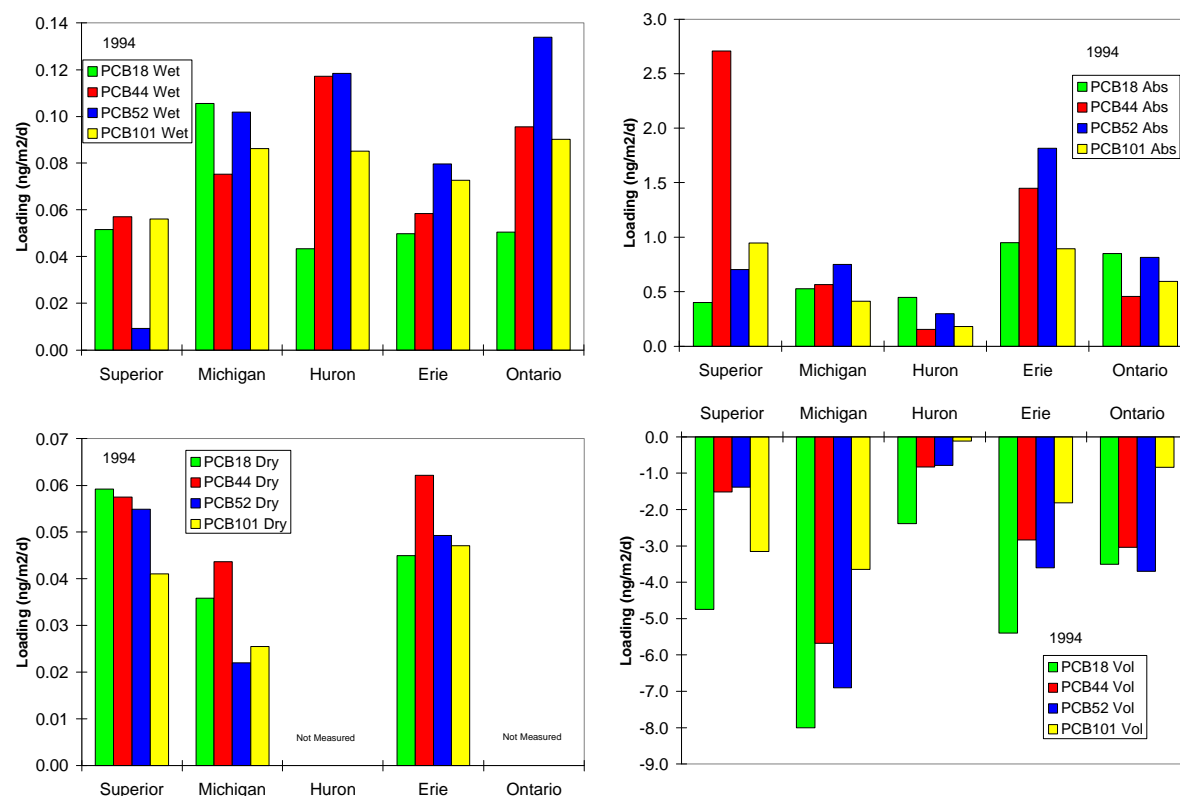


Figure II-13: As for Figure II.12, except for the PCB congeners.

A somewhat clearer spatial picture emerges for the PAHs and trace metals which are believed to have larger urban sources. For the PAHs (Figure II-14, left two panels), wet deposition shows a monotonic increase going from the upper to the lowest lake, which might be expected by the gradient in population. For dry deposition, Lake Erie has the largest flux for both PAHs, Pb, As, and Se and the proximity to Buffalo may be the reason for this (see the discussion of the paper by Gatz et al., 1995 and the paper of Blanchard et al., 1997). Cd shows no spatial differences in the wet deposition patterns.

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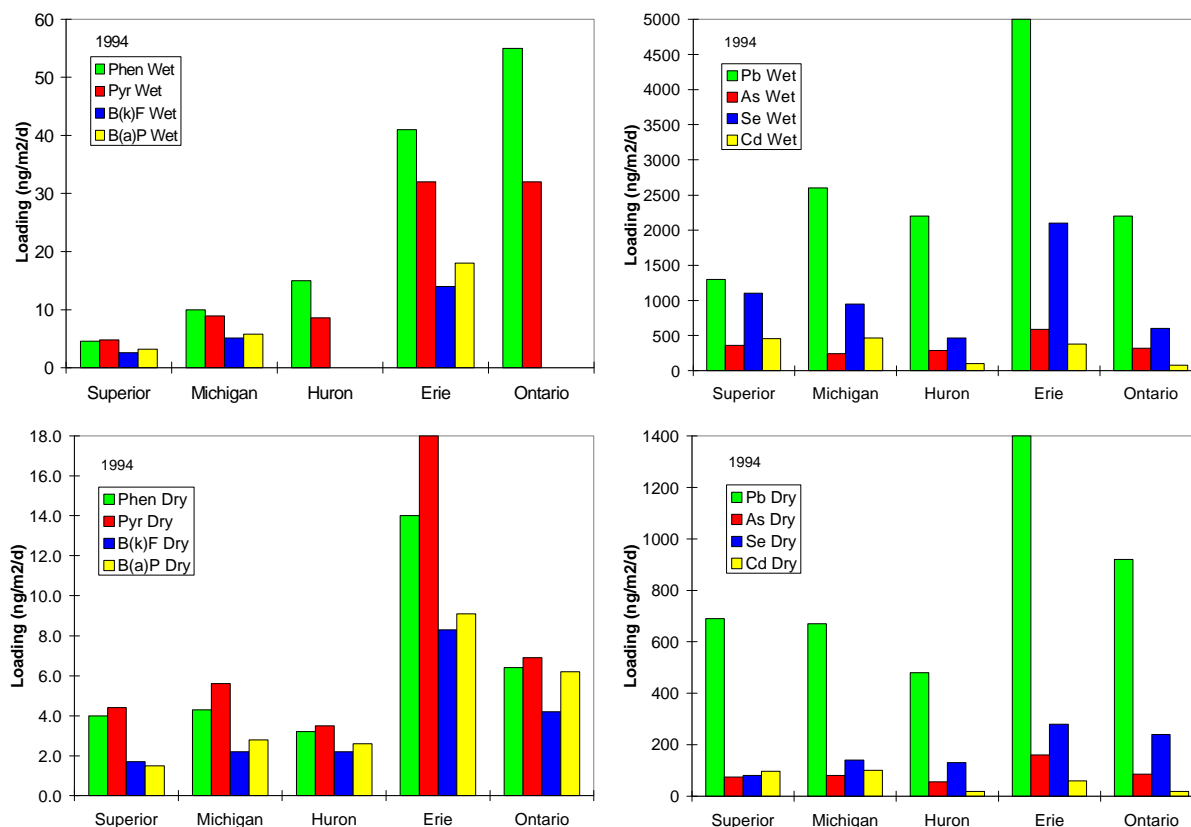


Figure II-14: Wet and dry deposition for the PAHs and trace metals by lake for the 1993 year.

For the other SVOCs, α -HCH (not shown here) indicates of a west to east gradient in the deposition fluxes, with the three lower lakes more intensely loaded than Superior and Michigan. γ -HCH has the highest wet deposition loading over Lake Huron and this may be indicative of a potential source in upper Michigan seen in other studies (Monosmith and Hermanson, 1996). Dieldrin wet deposition appears to be largest on the most urban lakes, Michigan and Erie.

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II.4 Extensions to IADN Data Analyses - Identification of Potential Sources

Annex 15 of the GLWQA called for the Parties to “develop models of the intermediate and long-range movement and transformation of toxic substances to determine; (i) the significance of atmospheric loadings to the Great Lakes System relative to other pathways; and (ii) the sources of such substances from outside the Great Lakes System”. While IADN has not included model development as part of its mandate, IADN researchers have used their data to infer sources of such chemicals from inside and outside the Great Lakes basin. These studies are not strictly part of IADN or required under IP1; however, these analyses are part of an effort by IADN Principal Investigators to extend the use of the IADN data beyond loading and trend studies.

II.4.1 Air trajectory analyses

It is known that many of the chemicals on the IADN measurement list are no longer currently in use and are part of the “global distillation” process described by Wania and Mackay (1994). Prior to IADN startup, data from measurements at the IADN satellite site at Egbert were used to infer sources of POPs using trajectory analysis of air motions on high and low concentration days (Hoff et al., 1991a, 1992b). The difficulty in this type of analysis is that air motions from the U.S and further south typically occur on warmer days, and warm days mean higher concentrations from the Clausius-Clapeyron equation (Equation II.1).

In 1993, toxaphene analyses from this 1989 study indicated five cases which were well above the expected concentration at the temperature of measurement, using the annual Clausius-Clapeyron behavior (Hoff et al., 1993a). Figure II-15 shows that these five high relative concentration cases at the Egbert site had strong air flow at 925 mb from the south, passing over regions which had considerable use of the chemical during the last year it was inventoried, 1980. Since that study, numerous examples of similar trajectory behavior have been seen in the examination of the IADN data. Back trajectories of p,p'-DDT are shown for the IADN Egbert and Point Petre stations in Figure II-16.

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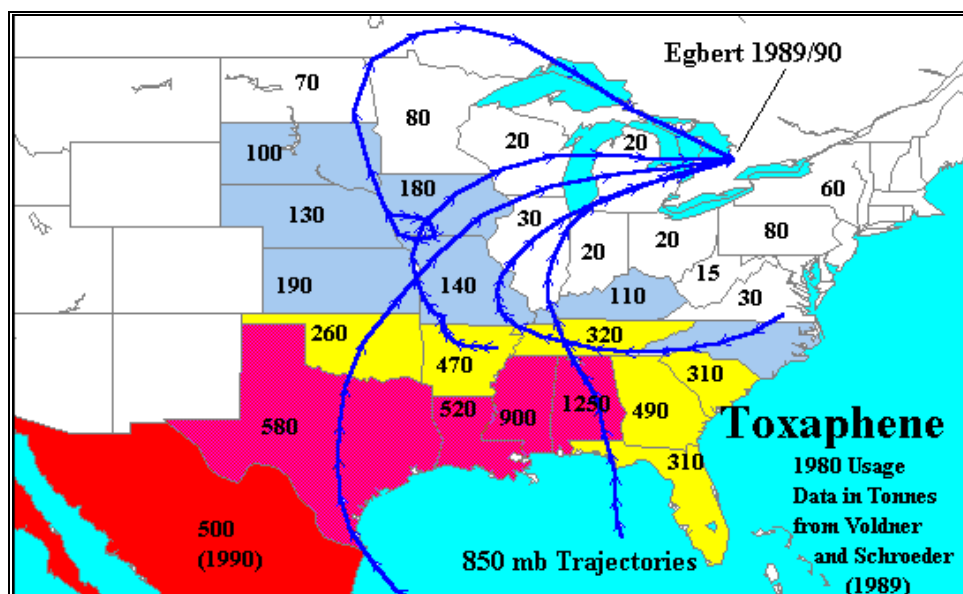


Figure II-15: Back trajectories at 850 mb showing potential sources of toxaphene to the IADN satellite site at Egbert, Ontario. The trajectories correspond to the five highest concentrations.

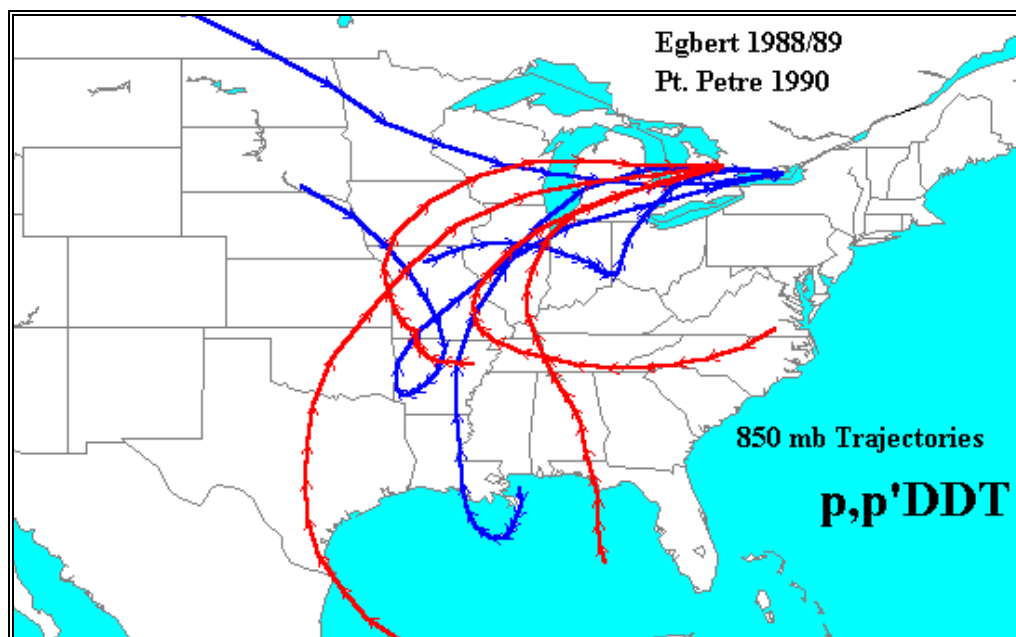


Figure II-16: Back trajectories at 850 mb showing potential sources of p,p'-DDT to the IADN sites at Egbert and Point Petre, Ontario. The four highest concentration cases from 1988/9 Egbert and Point Petre 1990 data are shown.

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Similar cases have been studied using more recent data (Hoff, IJC Presentation, 1997). Figure II-17 shows back trajectories for p,p'-DDT, endosulphan-I, γ -chlordane and dieldrin. Very similar trajectories (in fact many of the high concentration cases occur on the same days) are seen for DDT, chlordane and dieldrin. For endosulphan (a current use post-emergent pesticide), trajectories seem to pass over Michigan and Ontario. This would indicate that more local emissions are dominating the air concentrations. Ontario uses endosulphan widely on corn crops.

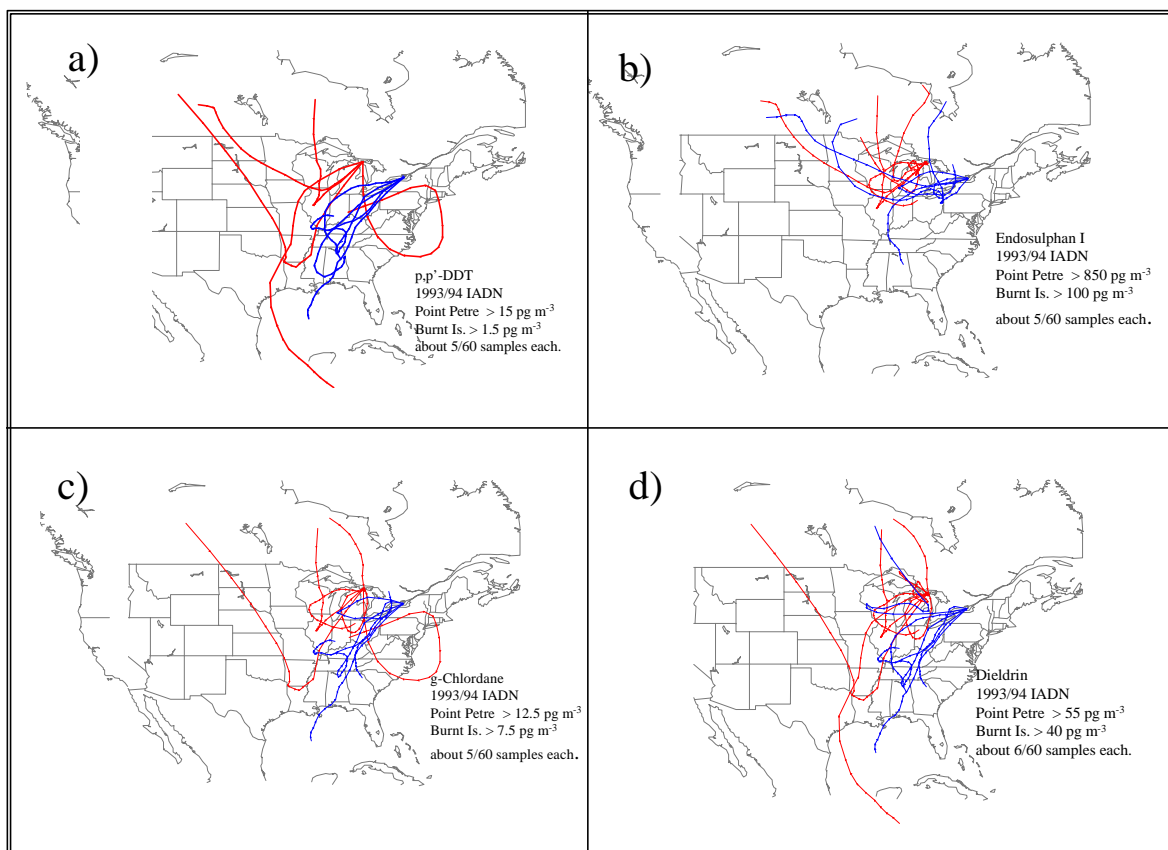


Figure II-17: Back trajectories for approximately the top 10th percentile of concentrations at the Burnt Island and Point Petre master stations for a)p,p'-DDT, b)endosulphan-I, c) g-chlordane, and d) dieldrin.

For some of the current use SVOCs and the heavy metals, the source identification story is quite different. In these cases, transport over the last 24 hours before sampling (and even the last six hours) is quite indicative of sources (Hoff et al., 1997; Blanchard et al., 1997). Figure

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II.18 shows the air trajectories for Pb, B(k)F and B(a)P using 1000 mb (surface level) trajectories. In all cases, urban areas are implicated as major sources. For the PAHs, however, the trajectories from Burnt Island indicate the Sault Ste. Marie area and there are major coking operations at steel mills in this region. For the metals, trajectories arriving at Point Petre have a strong signature from the Oswego/Syracuse, NY, direction and there is a major power plant near Oswego, NY, which is implicated. For Pb, the cities of Toronto, Hamilton and Buffalo are probable sources to Egbert, and it appears that Saginaw, MI, and Sudbury, ON, are sources to Burnt Island.

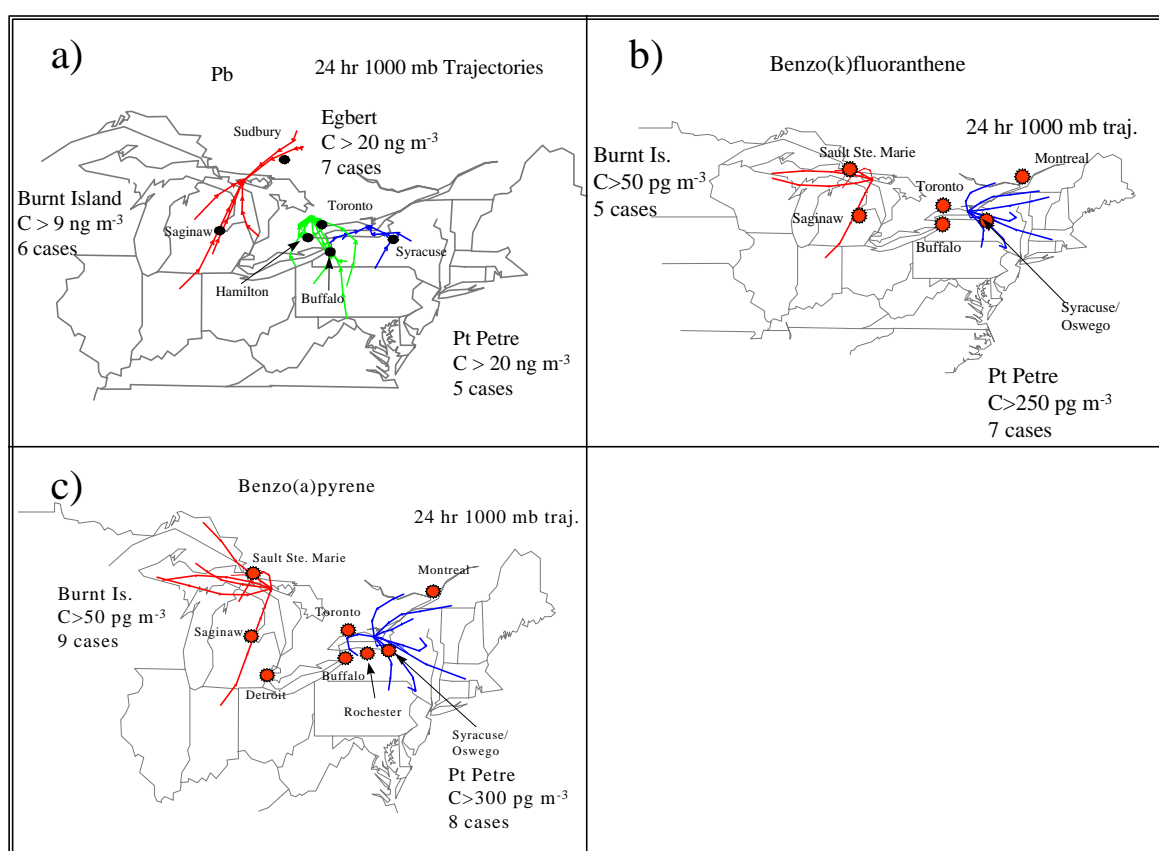


Figure II-18: 1000mb back trajectories for approximately the top 10th percentile of concentrations at the Burnt Island and Point Petre master stations for a)Pb, b)B(k)F, and c) B(a)P. Blue lines end at Point Petre, red lines at Burnt Island and green lines at Egbert, Ont.

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II.4.2 Potential Source Contribution Function and Principal Component Analyses

Use of the simplistic trajectory models is interesting but not conclusive, by any means. There is no way to determine where along a trajectory the chemical may have been introduced. Therefore, even though a trajectory may point back several hundreds to thousands of kilometers, sources near the site may, in fact, dominate. Use of more sophisticated treatments, such as conditional probability function analysis (Zeng and Hopke, 1989) has been tried (Biegalski, 1997a,b). In these works, bromine at Burnt Island has been postulated to arise in springtime from Arctic sources. A similar maximum in springtime has been seen in the high Arctic (Berg et al., 1983) and is believed to be due to biogenic sources. In another paper (Biegalski, 1997a), CPFA and principal component analysis were used to look at the metals from the Canadian sites, and industrial, urban, transportation, and natural sources were stratified. In a more recent study, Blanchard et al. (1997) apportioned not only the NAA metals, but also the ICP derived metals, and PAHS into a PCA scheme. Table II-16 shows the results of the PCA for Point Petre air data. The result of the analysis shows that the predominance of PAH emissions is from a signature which also includes Ni, V, and Pb. This combination is found in oil combustion. This may implicate stationary sources or diesel exhaust.

Gatz and Sweet (1995) analyzed U.S. IADN data and some Lake Michigan Mass Balance data using principle component analysis to explore groupings of pollutants in relation to meteorological conditions, in order to obtain clues about emission sources and processes. They found that, at the most urban site, high PAH loadings were related to winds coming from nearby Buffalo, indicating an urban source. PAH concentrations were not associated with any other pollutants, indicating unique PAH sources. PCBs, however, showed a weak association with pesticides, indicating possible similar sources of pesticides and PCBs, such as soils because of an association with temperature. The lack of association with wind direction further confirms that PCB sources are diffuse. Pesticide associations tend to vary with the site, suggesting the influence of local conditions (past use and management practices). A strong association between south winds and lindane, DDT, and dieldrin loadings was observed.

These techniques are only now beginning to be used with IADN data but future studies envisage the use of positive factor matrix correlation analysis, which will allow the combination

of time and concentration to be included as factors in the principal components. This technique will be useful in addressing trend information, allowing the use of variable weightings for missing or low confidence data. The technique also will enable source contribution by time to be investigated.

Table II-15: Varimax Rotated Principal Components, 1990-1994 Point Petre Trace Elements and PAH data. (Blanchard et al., 1997)

Variable	PC1	PC2	PC3	PC4	PC5	PC6	PC7	PC8
Ba		0.55	0.63					
Cd						0.91		
Mn		0.75	0.39					
Pb	(0.24)	0.38	0.48	0.33		0.48		
Ni	0.41	0.37					0.58	
Al		0.92						
As				0.73				
Br				0.76				
Ca		0.77	-0.35					
Ce		0.84						
Cl					0.86			
Fe		0.86	0.37					
Na					0.81			
Sb		0.33	0.68					
Se			0.67	0.40				
Th								0.94
Ti		0.83						
V	0.43	0.46					0.53	
Zn		0.45	0.62					
BaP	0.97							
BbF	0.98							
BeP	0.96							
BghiP	0.96							
BkF	0.97							
CHRY	0.98							
FLUORT	0.85							
INDENO	0.96							
PHEN	0.54			0.45			-0.45	
PYR	0.90							
Source?	Oil	Soil	Coal	Auto	Salt	Smelter?		Artif.

III. Where does IADN go from here?

This document is a discussion paper for review (especially for the IADN Peer Review) of the IADN program to date. The specific tasks to be addressed in the next period of IADN operations can be found in the Second Implementation Plan (IP2). The recommendations and suggestions here are only to be treated as guidance from the IADN Steering Committee. They do not supercede the IP2 and were made before IP2 was finalized.

III.1 Goal of the Second Implementation Plan (IP2)

The majority of IADN's monitoring activities, as outlined in Annex 15 of the Great Lakes Water Quality Agreement (GLWQA), were implemented during the tenure of the First Implementation Plan (IP1), 1990-1996. Because IP1 was somewhat ambitious in the number of operational, technical and research directives to be implemented, coupled with resource and program staging constraints, certain objectives were not fulfilled. Since these directives are fundamental to IADN's success in understanding the fate of persistent organic pollutants within the Great Lakes Basin, the shortcomings of IP1 need to be carried over and addressed during the Second Implementation Plan (IP2), scheduled for 1997-2003. The IP1 unaddressed topics, particularly unanswered science questions, are described in Section III.2.

Accordingly, **the goal of IADN during IP2 will be to continue to support Annex 15's surveillance and monitoring needs, conduct research to support that objective, and to provide credible scientific information for other related intergovernmental commitments and agreements, notably the Binational Great Lakes Toxics Strategy (BGLTS), Clean Air Act and the Canada-Ontario Agreement (COA).** The BGLTS states its objectives for the Parties, Environment Canada (and its partners) and the United States Environmental Protection Agency (and its partners):

- As a priority, co-ordinate efforts to identify sources of atmospheric pollutants in order to better define and co-ordinate emission control programs;
- Maintain atmospheric deposition monitoring stations to detect and quantify trends, deposition and transport of persistent toxic substances;

- Continue research on the atmospheric science of toxic pollutants to refine and improve existing source, receptor and deposition models, fundamental to impact assessment, while improving the integration of existing air toxic monitoring networks and data management systems to track deposition of contaminants within the Great Lakes;
- Conduct an impact assessment of the long range transport of persistent toxic substances from world-wide sources by 1998.

Fulfilment of these objectives will place the Parties in much better position to quantitatively determine temporal trends in deposition to the Great Lakes and to support management decisions, as called for in the BGLTS. The recommendations for what IADN should do during IP2, particularly the policy implications, are described in Section III.3.

III.2 Unresolved issues under IP1

The question remains as to whether IADN should remain strictly a surveillance/monitoring network as described in IP1 or whether it should also take more responsibility for the scientific research required Annex 15. This failure to act on the research component of Annex 15 was highlighted in a report, “The Progress of the Parties in Completing an Inventory of Toxic Air Emissions and in Assessing Toxic Air Deposition in the Lake Superior Basin” (IJC Air Quality Advisory Board, October 1993). There are responsibilities under Annex 15 (and the Binational Great Lakes Toxics Strategy) where IADN may logically take on additional research-related work (air-water exchange monitoring, for example) and some (transport modelling, health effects, regulatory controls) where it is not logical for a network to take the lead. There has been a considerable body of research which is relevant to Annex 15 conducted during the 1990-1996 period, but it has been largely parallel to and uncoordinated with IADN.

Within the US, parallel research during the first period of operation of IADN was quite active. The Green Bay Mass Balance project was completing its work about the time of the IADN start up. Lake Michigan Urban Air Toxics Study (LMUATS) and the Atmospheric Exchange over Lakes and Oceans (AEOLOS; Simcik et al., 1997) shed light on the urban plume influence from Chicago and the differences in air-water sampling. The LMUATS and the

AEOLOS studies included an IADN satellite station (IIT) and used Sleeping Bear Dunes as a background site. The more recent large scale Lake Michigan Mass Balance Project clearly addresses Annex 15 questions.

In Canada, a smaller scale research effort has been carried on in parallel to IADN, involving the use of buoys on the Great Lakes (Ridal et al., 1996a) and more recent, yet to be published work, pairs the over-water data with that from Point Petre (Bidleman, private communication). There have been a large number of process studies which have been carried out in the Great Lakes Basin looking at air-water exchange of toxaphene on Lake Superior (Jantunen and Bidleman, 1997), emissions inventories of toxics (Li et al., 1996), use of enantiomeric ratios of HCHs to infer fluxes of these chemicals from Lake Ontario (Ridal et al., 1996b), and others.

The establishment of the IADN network to conduct regular measurements of pollutants in air and precipitation for atmospheric deposition has been the major achievement of IP1. There are, however, several key areas of IP1 which have not been fulfilled.

There is a lack of progress on the appointment of QA/QC and database personnel. IP1 called for the establishment of a QA/QC manager (or one per country) to oversee the implementation of the QA plan. To date, no one is acting in that capacity. IP1 envisaged a database resident on one or both sides of the border and managed by a dedicated Database Manager. This individual was to receive biannual reports from each of the contributors to the IADN program and was to ensure that all of the data were processed into the same format and with the same data treatment. Resource limitations prevented this from occurring and the lack of progress in the database development reflects this. At present, all data are resident in agency flat files and there is as yet no relational database in place. Canada has committed to processing all Environment Canada data through the Research Data Management and Quality Control (RDMQ) system and to include that data in NATCHEM, Canada's air quality database. EPA has currently funded inclusion of the ISWS and Indiana University data into RDMQ, for future incorporation into NATCHEM. All work on this project is carried out on contract.

Another shortfall in the IP1 has been the lack of a routine and consistent inter-comparison of network data on an on-going basis. As well, replication at the Master stations only occurred for 1-3 years at the beginning of the IADN program, and co-location of samplers has been discontinued. It is important to ensure that early conclusions about inter-agency comparability

are still valid. One such example was the incompatibility of PCBs results in precipitation among agencies prior to 1994. Incompatibility was a result of various PCB reference standards and different methods used by different agencies. Associated with the PCB analysis is the question of what constitutes total PCBs. The original assumption was that a few congeners represent over 95% of the total PCB mass. There should be agreement on the list of predominant PCB congeners to quantify total PCBs. For example, in precipitation, IADN agencies uniformly and reliably detect (in over 75% of the samples) only 10 congeners. In air, about 40 congeners are seen with the same frequency. A workshop, including leading researchers on PCBs, would be one mechanism to recommend improved sampling and reporting requirements for PCBs. Reporting 100 or more additional congeners with low precision and compatibility does not improve knowledge about their levels in the environment. Within the Great Lakes Basin, there are other formal groups (Remedial Action Plans, RAPs; Lakewide Management Plans, LaMPs, etc.) working on GLWQA initiatives. Informal contact has been made with some RAP and LaMP personnel and it is suggested that more formal contact be maintained.

III.3 Recommendations for IP2

There is agreement among the members of the binational IADN Steering Committee that IADN must continue to do what it does well – measure concentrations and report on loadings/fluxes of contaminants to the Great Lakes. Information on trends in atmospheric concentrations and loadings will contribute to tracking binational, indeed global, efforts to reduce toxics. At the same time, there is an opportunity to move forward, both in terms of advancing our understanding of atmospheric processes, and in responding to the emerging needs of the Parties in delivering, for example, the Binational Great Lakes Toxics Strategy.

III.3.1 Recommendations to improve measuring and reporting

It is critical that IADN produce reliable, compatible data. To this end, **the Quality Assurance Program Plan (QAPP) needs to be regularly updated and implemented** as agreed, under the direction of the **QA Manager**. To ensure that protocols are being adhered to, **quarterly audits** of field and laboratory operations are recommended. In addition, there need to be regular **binational QA/QC studies**. A thorough **analysis of the historical database** which resulted from colocation of samplers at Point Petre should be done. The concept of Master Stations, wherein all parties participating in IADN operate **colocated samplers**, should be

continued at one site [recommend Point Petre, since highest current level of participation at that site] so that compatibility of resultant data can be constantly reassessed. In addition, **periodic data review workshops** should be held.

It is recognized that the delay in publishing atmospheric loading estimates (for example, in 1997 reporting 1994 data) is unacceptably long. There are two reasons for this: analytical turnaround time, and data processing time. It may be possible to lower the number of analytes in the IADN list if they are no longer scientifically required. However, this runs counter to the expected requirement for more chemicals, not fewer, to be monitored. Clearly, the discussion of the number of PCB congeners analysed and reported is relevant to this problem. With the potential addition of other complex species, toxaphene or the chlorinated naphthalenes, the analyte list could grow exponentially.

If **samples of larger volume** were obtained, the laboratory analysis would be less time consuming since the concentrations would be well above blank levels. It may also be possible that **improved analytical techniques** that might be more efficient.

Data and quality assurance time is proportional to the number of chemicals analysed as well. Data processing would be improved if all data were stored on a **single database** (as a minimum, if all Canadian data were maintained on a single database), in the format specified in the QAPP. This would be facilitated by hiring a **Data Manager**, who would be responsible for maintaining this database (including metadata, i.e. the “data about the data”).

With the increased recognition of the importance of atmospheric sources to various initiatives (eg., Lakewide Management Plans, Remedial Action Plans, Binational Great Lakes Toxics Strategy, Mass Balance models on lakes Michigan and Ontario), sharing of information becomes a key consideration. It is recommended that an internet **web site** be established (and linked to appropriate key sites), and include appropriate fact sheets (for public consumption), data summaries, latest loadings estimates and how they were derived, list of contacts, etc. The Data Manager would also be responsible for maintaining the currency of this site.

As called for in the first implementation plan, an IADN Working Group established a parameter list in 1989. The **parameter list**, based on the Great Lakes Water Quality Board list of critical pollutants, was selected based on: analytical feasibility, suspected atmospheric source, and bioaccumulative/toxicological properties. It is necessary to **update this list** to include the

critical pollutant lists of the various LaMPs, as well as other binational/global initiatives such as the Binational Great Lakes Toxics Strategy, UNECE and NAFTA CEC. Possibly, IADN should also be monitoring for in-use pesticides. Furthermore, in an effort to detect emerging issues, **gas chromatography/mass spectroscopy scans** should be performed on selected ampoules of historical sample extracts, as well as, routinely, on a limited number of current sample extracts. This will allow IADN to address potential chemicals of concern, as required by the LaMPs.

III.3.2 Recommendations to improve our understanding of atmospheric processes

Success in decontaminating or restoring the Great Lakes is becoming increasingly dependent on atmospheric concentrations and thus on the processes which determine these concentrations (Mackay and Bentzen, 1997). To quantify the direction and magnitude of flux with greater accuracy, there is a need for **concurrent measurements of concentrations in both air and water** as a function of time during the entire year (at a minimum, during spring and summer), as well as for more accurate determination of **air-water partition coefficients** (including their temperature dependence) and the extent of sorption to particulate matter in both air and water.

One of the underlying assumptions in IADN is that measurements on shore are representative of deposition in the open lakes. This assumption has not been validated. There are infrequent measurements made on research vessels in the open lakes, but there has not been a comprehensive study to address differences in **over-land/over-water** atmospheric concentrations and fluxes of toxic organic chemicals.

With many large urban centers in the Great Lakes, the contribution of pollutants from the these centers should not be ignored. Recent studies from AEOLUS off Chicago/Gary showed large concentration gradients of PCBs and PAHs from urban areas to the lake. A specific research question to be addressed is the importance of urban areas to the overall lakewide impact of airborne toxics. To this end, we recommend that **paired urban/remote measurements** be made at one location in Canada (Toronto/Point Petre) and one in US (Chicago/Indiana Dunes or Sturgeon Point/Buffalo) to determine the scale of this problem.

Estimates of dry deposition of pollutants are indirectly modeled from other measurements. These models are highly dependent on particle size distribution, gas-particle distribution of toxic chemicals, and deposition velocities. **Physical constants** such as Henry's

Law constants, mass transfer coefficients, deposition velocities, etc. are critical parameters used in the mass balance models. The removal rate and the recycling of many OCs and PCBs in the environment will largely determine whether the Great Lakes act as a reservoir or source. These rates are governed by the **chemical and physical properties** of the toxic pollutants. Research should be conducted to determine these constants and reduce the uncertainties in mass balance models. **Air/vegetation, water/sediment, air/soil exchanges should be determined** as part of understanding these competing processes with air/water exchange.

Linking air pollution with sources is a complicated task, because air pollution at any one location usually consists of a mixture of chemicals released from many sources. Many of the OCs have long been banned or regulated for use in North America, although some of these chemicals are still being used in countries outside of continental America. Source apportionment is further complicated by complex and ever-changing weather conditions, variations in emissions from a given source, and changes in the chemical and physical forms of pollutants as they move through the atmosphere. A variety of mathematical models are used to determine what sources are contributing most to air pollution to the Great Lakes. By working collaboratively with other researchers studying atmospheric processes, there is a greater possibility of making some source/receptor linkages. Therefore, it is recommended that IADN **develop stronger ties** with other regional networks, including the Northern Contaminants Program (NCP). For example, there is presently an NCP proposal to study the presence of selected “new” chemicals (such as chlorinated paraffins; brominated diphenyl ethers; OC/OP insecticides – eg., chlorpyrifos; herbicides/fungicides – eg., atrazine, dacthal, pentachloronitrobenzene) in Arctic air, water and marine mammal extracts. By measuring these chemicals in the Great Lakes Basin, IADN could provide a “near source” signature, as well as contribute to the determination of south/north concentration gradients, and differential deposition of the various chemicals under different temperature regimes.

In terms of other national and international networks, the U.S. foresees the need to use IADN as a template for expansion of air toxics monitoring across the nation, and for use in international monitoring efforts, such as the NAFTA CEC.

Pesticide **enantiometric ratios** show promise for determining source characterization of these chemicals, whether they be from current or past use through soil volatilization. These types of tracer techniques should be investigated.

One research topic which has not been addressed in IADN but could be investigated is the **precipitation scavenging processes** and whether the washout ratios computed from the IADN data are consistent with those from other programs, such as the Chesapeake Bay project. If they are not, investigations should be conducted to determine why not; if they are, these results should be conveyed to the removal codes in the atmospheric transport models.

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Appendix A

ANNEX 15 - AIRBORNE TOXIC SUBSTANCES

1. **Purpose.** The Parties, in cooperation with State and Provincial Governments, shall conduct research, surveillance and monitoring and implement pollution control measures for the purpose of reducing atmospheric deposition of toxic substances, particularly persistent toxic substances, to the Great Lakes Basin Ecosystem.

2. **Research.** Research activities shall be conducted to determine pathways, fate and effects of such toxic substances for the protection of the Great Lakes System. In particular, research shall be conducted to:
 - a) understand the processes of wet and dry deposition and those associated with the vapor exchange of toxic substances;
 - b) understand the effects of persistent toxic substances, singly or in synergistic or additive combination with other substances, through aquatic exposure routes on the health of humans and the quality and health of aquatic life where a significant source of these substances is the atmosphere, in accordance with sub-paragraph 4(b) of Annex 12;
 - c) develop models of the intermediate and long-range movement and transformation of toxic substances to determine;
 - i) the significance of atmospheric loadings to the Great Lakes System relative to other pathways; and
 - ii) the sources of such substances from outside the Great Lakes System.

3. **Surveillance and Monitoring.** The Parties shall:
 - a) establish, as part of the Great Lakes International Surveillance Plan (GLISP) instituted under Annex 11, an Integrated Atmospheric Deposition Network in accordance with paragraph 4 below;
 - b) identify, by means of this Network, toxic substances and, in particular, persistent toxic substances, appearing on List No. 1 described in Annex 1, of those designated as Critical Pollutants pursuant to Annex 2 and their significant sources in accordance with sub-paragraph 4(c) of Annex 12, and to track their movements; and
 - c) utilize this Network in order to:
 - i) determine atmospheric loadings of toxic substances to the Great Lakes System by quantifying the total and net atmospheric input of these same contaminants, pursuant to sub-paragraph 3(a) of Annex 11;
 - ii) define the temporal and spatial trends in the atmospheric deposition of such toxic substances in accordance with sub-paragraph 4(a) of Annex 12; and
 - iii) develop Remedial Action Plans and Lakewide Management Plans pursuant to Annex 2.

4. **Components of the Integrated Atmospheric Deposition Network.** The Parties shall confer on or before October 1, 1988, regarding;
 - a) the identity of the toxic substances to be monitored;
 - b) the number of monitoring and surveillance stations;
 - c) the locations of such stations;
 - d) the equipment at such stations;
 - e) quality control and quality assurance procedures; and
 - f) a schedule for the construction and commencement of the operation of the stations.
5. **Pollution Control Measures.** The Parties, in cooperation with State and Provincial Governments, shall develop, adopt and implement measures for the control of the sources of emissions of toxic substances and the elimination of the sources of emissions of persistent toxic substances in cases where atmospheric deposition of these substances, singly or in synergistic or additive combination with other substances, significantly contributes to pollution of the Great Lakes System. Where such contributions arise from sources beyond the jurisdiction of the Parties,
 - a) the Parties shall notify the responsible jurisdiction and the Commission of the problem and seek a suitable response.
 - b) The Parties shall also assess and encourage the development of pollution control technologies and alternative products to reduce the effect of airborne toxic substances on the Great Lakes System.
6. **Reporting.** The Parties shall report their progress in implementing this Annex to the Commission biennially, commencing with a report no later than December 31, 1988.

Appendix B

IADN Related Presentations

Basu, I., M. Tankard, R. A. Hites, "Analysis of organochlorine pesticides in air and precipitation samples from Great Lakes shore-line sites", International Association for Great Lakes Research Meeting, Toronto, Canada, May 1996

Basu, I., J. F. Wallace., R. A. Hites, "High PCB concentration in indoor air may pose contamination problems for sample collection and analysis", International Association for Great Lakes Research Meeting, East Lansing, MI, May 1995

Biegalski, S. R., Landsberger, S., Hoff, R.M. and K. A. Brice, "Source-receptor Modeling using Trace Elements in Aerosols Collected at Burnt Island, Egbert, and Point Petre", Int. Assoc. Great Lakes Res. Meeting, Lansing MI, June 1995.

Blanchard, P., J. F. Hopper and R. M. Hoff, "Analysis of Organic Aerosol Constituents Collected at a Rural Site in Southern Ontario", Air-Waste Man. Assoc. Annual Meeting, Dallas, TX, June 1995

Cortes, D.R., R. A. Hites, "Meteorological influences on atmospheric concentrations of polycyclic aromatic hydrocarbons at Sturgeon Point, New York", 19th Midwest Environmental Chemistry Workshop, West Lafayette, IN, October 1996

Cortes, D.R., R. A. Hites, "Temporal trends in gas-phase concentrations of organochlorine pesticides measured at Lakes Superior, Michigan, and Erie", International Association of Great Lakes Research Meeting, Buffalo, NY, June 1997

Cortes, D.R., B. R. Hillery, R. A. Hites, "Temporal trends in the atmospheric concentrations of selected polycyclic aromatic hydrocarbons measured on the eastern shore of Lake Erie", International Association for Great Lakes Research Meeting, Toronto, Canada, May 1996

Hillery, B. R., I. Basu, R. A. Hites, "Organic contaminants in air and precipitation at three sites on the Great Lakes", International Association for Great Lakes Research Meeting, East Lansing, MI, May 1995

Hillery, B. R., I. Basu, R. A. Hites, "Temporal and spatial variation in organic contaminants at three sites on the Great Lakes", Society for Environmental Chemistry and Toxicology, Ohio Valley Chapter, Miami, OH, June 1995

Hillery, B. R., I. Basu, R. A. Hites, "The effect of temperature and wind speed on vapor phase concentrations of polychlorinated biphenyls in air near the Great Lakes", International Association for Great Lakes Research Meeting, Toronto, Canada, May 1996

Hillery, B. R., R. A. Hites “Temporal trends in a long-term study of vapor phase PCB concentrations near the Great Lakes”, 16th Symposium on Chlorinated Dioxins and Related Compounds, Amsterdam, The Netherlands, August 1996

Hillery, B. R., I. Basu, R. A. Hites, “Temporal trends in the vapor phase concentrations of semi-volatile organics in air near the Great Lakes”, Atmospheric Deposition to the Great Waters, Air and Waste Management Association, Niagara Falls, NY, October 1996

Hillery, B. R., “Atmospheric concentrations of PCBs near the Great Lakes”, University of Maine, Department of Chemistry, Orono, Maine, November 1996

Hillery, B. R., “Temporal trends in the vapor phase concentrations of semi-volatile organics in air near the Great Lakes”, Indiana University, School of Public and Environmental Affairs, Bloomington, IN, November 1996

Hillery, B. R., R. Hoff, R. A. Hites, “Atmospheric contaminant deposition to the Great Lakes determined from the Integrated Atmospheric Deposition Network”, In Atmospheric Deposition of Contaminants to the Great Lakes and Coastal Waters, J. E. Baker, editor, Chapter 16 (1997)

Hillery, B. R., I. Basu, C. W. Sweet, R. A. Hites, “Temporal and spatial trends in a long term study of gas-phase PCB concentrations near the Great Lakes,” Environmental Science and Technology, 31, 1811-1816 (1997)

Hillery, B. R., I. Basu, R. A. Hites, “Concentrations of PCBs in precipitation and particles phases in air near the Great Lakes”, International Association of Great Lakes Research Meeting, Buffalo, NY, June 1997

Hillery, B. R., I. Basu, R. A. Hites, “Atmospheric concentrations of atrazine, trans-nonachlor, and dieldrin at Sleeping Bear Dunes, Michigan”, International Association of Great Lakes Research Meeting, Buffalo, NY, June 1997.

Hites, R. A., “Temporal and spatial variation in organic contaminants at three sites on the Great Lakes”, Third Annual Lake Michigan Mass Balance Meeting, Chicago, IL, December, 1996

Hites, R. A., I. Basu, “Time-series analysis of PCB concentrations at Sleeping Bear Dunes”, Second Annual Lake Michigan Mass Balance Meeting, Chicago, IL, December, 1995

Hites, R. A., “Atmospheric chemistry of PCBs”, DePauw University, Division of Sciences and Department of Chemistry, Greencastle, IN, October 1996

Hites, R. A., “Atmospheric chemistry of PCBs”, California Institute of Technology, Department of Environmental Engineering Sciences, Pasadena, CA, November 1996

Hoff, R. M. "Updated Atmospheric Loading Estimates of 11 Organics, 4 PAHs and 5 Trace Metals to the Great Lakes", International Association of Great Lakes Research, Mississauga,

Ontario, June 1996.

Hoff, R. M. "Monitoring Efforts", International Joint Commission Biennial Meeting, Duluth, MN Sept. 1995 (INVITED).

Hoff, R. M. "Integrated Atmospheric Deposition Network", U.S. E. P. A. Lake Michigan Mass Balance Workshop, Detroit, MI, June 1995 (INVITED).

Hoff, R. M. "Error Estimates in Mass Balances", U.S. E. P. A. Lake Michigan Mass Balance Workshop, Detroit, MI, June 1995 (INVITED).

Hoff, R.M, C. H. Chan, W. M. J. Strachan, J. Bode, D. Gatz, C. Sweet, M. Shackleton "Atmospheric Contaminant Deposition to the Great Lakes Determined from the Integrated Atmospheric Deposition Network (IADN), Soc. Env. Toxicol. and Cont., Denver CO, November 1994.

Hoff, R.M., K. A. Brice, W. M. J. Strachan and M. Shackleton, "Deposition of Trace Metals to the Great Lakes", Inter. Assoc. of Great Lakes Res. Annual Meeting, Windsor, ON, June 1994.

Hoff, R.M., "Air Toxics Transport and Effect on the Great Lakes", Symposium on Remediation of the Great Lakes, Michigan State U., Lansing, MI, Mar. 94 (INVITED).

Hoff, R.M., "Vapour/Particle Exchange", CIRAC/AWMA Topical Meeting on Air Toxics Processes, Toronto, Jan. 1994 (INVITED).

Hoff, R.M., "Results from the Canadian IADN Program", U.S.EPA/ Environment Canada Binational Meeting on the Great Lakes Water Quality Agreement Annex 15 Progress, Nov. 1993, Toronto.

Hoff, R.M., "Results from the Canadian IADN Network", Pritzger Department of Environmental Engineering, Illinois Institute of Technology, Feb. 1993. (INVITED)

Hoff, R. M., "Measurement of PCCs in Air in Southern Ontario", Toxaphene Workshop, NWRI/AES, Burlington, ON, Feb. 1993.

Hoff, R. M., 1997. What do the slopes of the antoine plot of air concentrations tell us about processes of air-surface exchange? International Association of Great Lakes Research Annual Meeting, Buffalo, NY, May 30-June 4, 1997.

Hoff, R. M. , P. Blanchard and J. F. Hopper, 1997. Sources of atmospheric polynuclear aromatic hydrocarbons and trace metals over Lake Ontario. International Association of Great Lakes Research Annual Meeting, Buffalo, NY, May 30-June 4, 1997.

Muir, D. C. G., N. P. Grift, E. Fee, R. M. Hoff, W. M. J. Strachan, Atmospheric Loadings and Bioaccumulation of PCBs and Current Use Pesticides in Lake Nipigon and other Lakes in Northwestern Ontario, Int. Assoc. Gt. Lakes Res. Annual Meeting, Green Bay, WI, June 1993.

Ramsey, B., M. C. Wassouf "Total suspended particle and total organic carbon (TSP and TOC) analysis", Indiana University Undergraduate Thesis, May 1995

Strachan, W. M. J., Burniston, D. A., Hoff, R.M., L'Italien, S. and K. W. Kuntz "Mass Balance of Persistent Organic Pollutants in Lake Ontario (1990)", Int. Assoc. Great Lakes Res. Meeting, Lansing MI, June 1995.

Tankard, M. W. "Analysis of organochlorine pesticides in atmospheric samples near Lakes Superior, Michigan, and Erie", Indiana University Master of Science Thesis, August, 1996